

**SYNTHESIS AND FREE RADICAL DECARBONYLATION
OF SOME SMALL-RING ALDEHYDES**

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ABSTRACT

A number of small-ring radicals have been generated by peroxide-initiated decarbonylation of the appropriate aldehydes, neat and in diphenyl ether, and the extent of rearrangement in these reactions has been determined in each case. The results are compared with known examples of free radical rearrangements and with rearrangements which occur in carbonium ion reactions in the same small-ring systems. The results are found to be in accord with the predictions of simple molecular orbital (L.C.A.O.) theory.

No decarbonylation of cyclopropanecarboxaldehyde was observed. 1-Methyl- and 1-phenylcyclopropanecarboxaldehyde gave exclusively methyl- and phenylcyclopropane, respectively, on decarbonylation. Cyclobutanecarboxaldehyde, cyclopropylacetaldehyde and dimethylcyclopropylacetaldehyde afforded exclusively cyclobutane, 1-butene and 2-methyl-2-pentene, respectively, on decarbonylation. A mixture of 2-methyl-2-pentene and isopropylcyclopropane was obtained on decarbonylation of dimethylcyclopropylacetaldehyde in benzyl mercaptan.

The possible role of "non-classical" homoallylic radical intermediates in the free radical reactions of cyclopropylcarbinyl derivatives is discussed. A decision could not be made on the basis of available evidence between mechanisms involving classical and "non-classical" radical intermediates in these reactions. The evidence

does suggest that "non-classical" bicyclobutonium radical intermediates are not important in these reactions.

The methods of synthesis of the small-ring aldehydes used in this study are presented and discussed.

TABLE OF CONTENTS

PART	TITLE	PAGE
I.	INTRODUCTION	1
	Free Radical Rearrangements	1
	Carbonium Ion and Carbanion Rearrangements in Small-Ring Systems	18
	Free Radicals in Small-Ring Systems	23
II.	RESULTS AND DISCUSSION	38
	Synthetic Methods	38
	Decarbonylation Results	49
	Discussion of the Decarbonylation Results	53
	A. Cyclopropanecarboxaldehyde, 1-Methyl- cyclopropanecarboxaldehyde and 1-Phenyl- cyclopropanecarboxaldehyde	53
	B. Cyclobutanecarboxaldehyde, Cyclopropyl- acetaldehyde and Dimethylcyclopropyl- acetaldehyde	63
	General Comments	81
III.	EXPERIMENTAL	83
	Cyclopropanecarboxaldehyde	84
	1-Phenylcyclopropanecarbonitrile	85
	1-Phenylcyclopropanecarboxaldehyde	86
	(1-Phenylcyclopropyl)-carbinylamine	88
	3-Methyl-3-cyanopyrazoline	90
	1-Methylcyclopropanecarbonitrile	90
	1-Methylcyclopropanecarboxaldehyde	92
	Zinc-Copper Couple	93
	Bicyclo[4.1.0]heptane	94
	Phenylcyclopropane from Styrene	95
	Cyclopropylacetonitrile from Allyl Cyanide (Attempted)	96
	Allylcarbinol	96
	2-Cyclopropylethanol from Allylcarbinol (Attempted)	96
	Allylcarbinyl Acetate	97
	2-Cyclopropylethyl Acetate from Allylcarbinyl Acetate	97
	3-Butenal Dimethyl Acetal	99

PART	TITLE	PAGE
III.	3-Butenal Diethyl Acetal	101
(cont'd.)	3-Methyl-3-butenal Diethyl Acetal	102
	3-Methyl-3-butenal Dimethyl Acetal	103
	Cyclopropylacetaldehyde Diethyl Acetal from 3-Butenal Diethyl Acetal (Attempted)	104
	Cyclopropylacetaldehyde Dimethyl Acetal from 3-Butenal Dimethyl Acetal (Attempted)	104
	(1-Methylcyclopropyl)-acetaldehyde Dimethyl and Diethyl Acetals (Attempted)	106
	Methyl Cyclopropylacetate	106
	2-Cyclopropylethanol	108
	2-Cyclopropylethanol from Cyclopropyl Chloride (Attempted)	109
	N,N-Dimethylcyclopropylacetamide	110
	Cyclopropylacetaldehyde I. Reduction of N,N-Dimethylcyclopropylacetamide	113
	Cyclopropylcarbinol	117
	Cyclobutanol	118
	Cyclopropylcarbinol and Phosphorous Tribromide	118
	Cyclopropylacetonitrile (Cyclopropylcarbinyl Cyanide)	119
	Cyclopropylacetaldehyde. Reduction of Cyclo- propylacetonitrile (Attempted)	122
	Allylcyclopropane	123
	3-Cyclopropyl-1,2-propanediol	125
	Cyclopropylacetaldehyde II. Cleavage of 3-Cyclopropyl-1,2-propanediol	127
	Cyclobutanecarboxylic Acid	131
	Cyclobutylcarbinol	131
	Cyclobutanecarboxaldehyde I. Oxidation of Cyclobutylcarbinol	131
	Cyclobutanecarbonyl Chloride	133
	N-Methylcyclobutanecarboxanilide	133
	Cyclobutanecarboxaldehyde II. Reduction of N-Methylcyclobutanecarboxanilide	134
	Dimethylcyclopropylacetonitrile	138
	Dimethylcyclopropylacetaldehyde	139
	Ethyl Cyclopropanecarboxylate	141
	Dimethylcyclopropylcarbinol	141
	Isopropenylcyclopropane	141
	Isopropylcyclopropane	142
	Decarbonylation Experiments. General Procedure	144

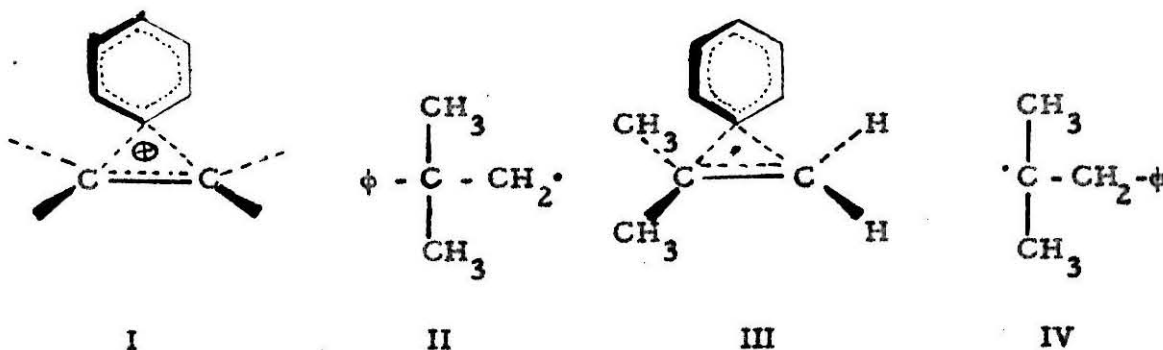
PART	TITLE	PAGE
III. (cont'd.)	Decarbonylation of Cyclopropanecarbox- aldehyde	146
	Decarbonylation of 1-Methylcyclopropane- carboxaldehyde	148
	Decarbonylation of 1-Phenylcyclopropane- carboxaldehyde	150
	Decarbonylation of Cyclobutanecarbox- aldehyde	152
	Decarbonylation of Cyclopropylacetaldehyde	153
	Decarbonylation of Isovaleraldehyde	155
	Decarbonylation of a Mixture of Cyclopropyl- acetaldehyde and Isovaleraldehyde	156
	Decarbonylation of Dimethylcyclopropyl- acetaldehyde	157
IV.	REFERENCES	161
V.	PROPOSITIONS	170
VI.	REFERENCES FOR PROPOSITIONS	180

I. INTRODUCTION

Free Radical Rearrangements

In comparison with the large number of molecular rearrangements which have been observed in reactions occurring via carbonium ion intermediates, relatively few rearrangements have been observed in reactions occurring via carbanion or free radical intermediates. Investigators have generally looked for carbanion and free radical rearrangements in systems which are known to undergo carbonium ion rearrangements. This has therefore led to studies of free radical reactions in phenylethyl, neopentyl and some bicyclic systems, systems which are known to undergo extensive rearrangements in carbonium ion reactions and in some of which "non-classical" carbonium ions have been postulated as reaction intermediates. Extensive carbonium ion rearrangements are also known to occur in the interconversion of cyclopropylcarbinyl, cyclobutyl and allylcarbinyl derivatives and these reactions have recently been studied very thoroughly (1). However, relatively little work has been done on free radical and carbanion reactions in these small-ring systems. This thesis involves a study of free radical reactions in small-ring systems and particular attention has been directed to the determination of the extent of rearrangement in these reactions.

Historically, the first cases of free radical rearrangements which were studied in detail involved the 1,2-migration of phenyl groups in neophyl (2,2-dimethyl-2-phenylethyl) systems. These rearrangements are analogous to the well-known 1,2-migrations of phenyl groups in substituted and unsubstituted β -phenylethyl carbonium ions for which unsymmetrical and symmetrical bridged "non-classical" phenonium ions I have been postulated as reaction intermediates (2).

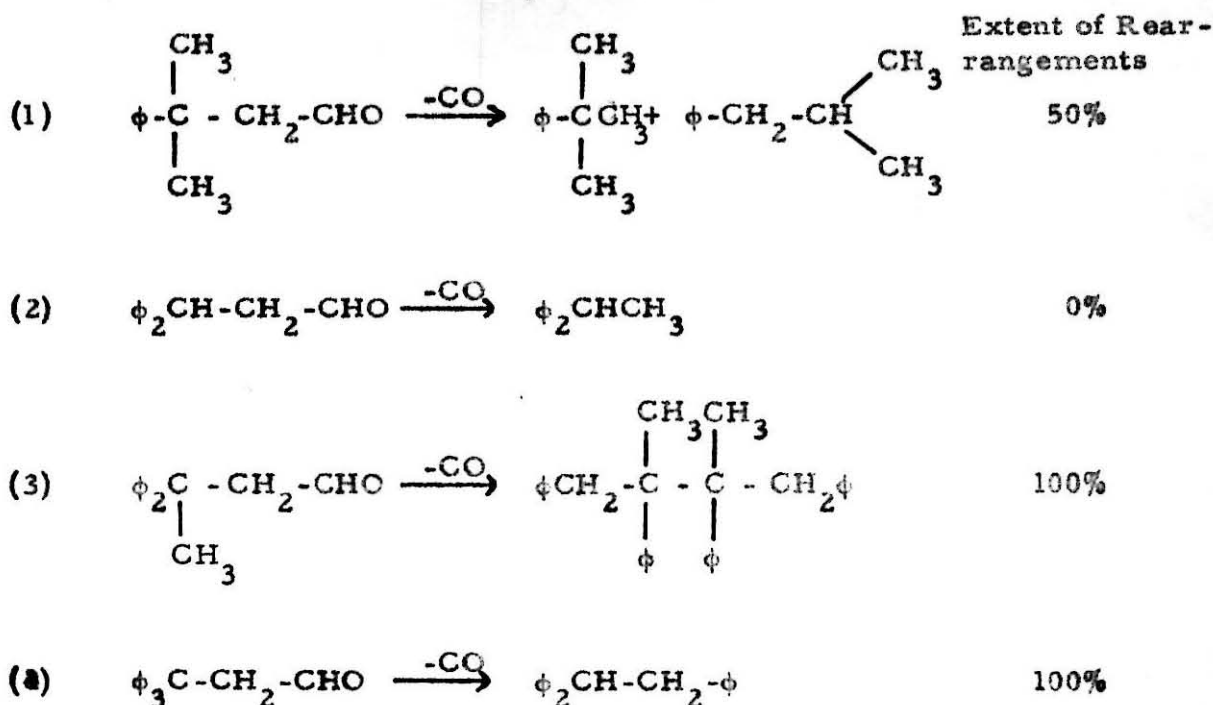


When the neophyl radical II was generated by the reaction of neophyl chloride with either phenylmagnesium bromide or *n*-butylmagnesium bromide and a trace of cobaltous chloride (3), the products contained a mixture of *t*-butyl- and *i*-butylbenzene. The di-*t*-butyl peroxide-initiated decarbonylation of 3-phenyl-3-methylbutanal (neophylcarboxaldehyde)(4) gave a 1:1 mixture of *t*-butyl- and *i*-butylbenzene but no *s*-butylbenzene. By changing the concentration of neophylcarboxaldehyde in the decarbonylation reaction, Seubold (5) observed that the ratio of the rearranged to unrearranged products changed, indicating that two distinct classical radicals, II and IV, were involved as intermediates. A bridged "non-classical" radical III, analogous to I above, would be expected to react

with a given reagent so as to give a constant ratio of rearranged and unrearranged products, independent of the concentration of the reagent. A bridged radical such as III could, however, represent the transition state for conversion of II to IV. Seubold also suggested (5) that the activation energy for rearrangement of the phenyl group is 7-8 kcal/mole.

Recently, Ingold and his co-workers studied the chlorination of t-butylbenzene over the temperature range 190-245° (6). Since it is known that the individual steps in a long-chain radical chlorination process are very fast (7), these workers were interested in determining whether the initially formed neophyl radical would have time to rearrange, as in the reactions reported above. They found (6) that the complex reaction mixture contained neophyl chloride and 2-benzylpropyl chloride in a ratio of 5:1, in addition to olefins, polychlorinated products and recovered starting material. While the extent of rearrangement was substantially reduced in the chlorination reaction as compared to the decarbonylation reaction, rearrangement was still observed. This result indicates that the rearrangement step must have been very fast at these temperatures in order to compete so well with the reaction of chlorine with unrearranged neophyl radicals.

According to the work of Curtin and Hurwitz (8), the extent of rearrangement in neophyl-type systems changed as the methyl groups were successively replaced by phenyl groups.

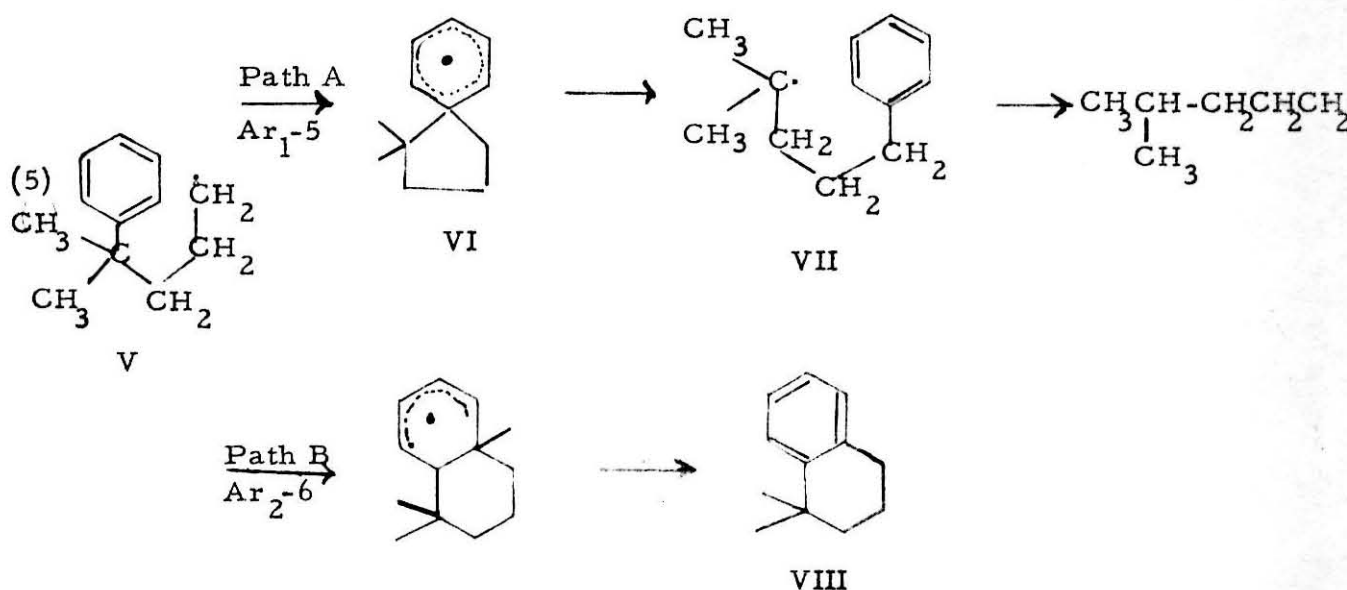


Curtin and Kauer (9) were able to show by deuterium labeling that the lack of phenyl rearrangement in reaction (2) was not due to competitive hydrogen migration since no deuterium shuffling was observed. They postulated that the different degrees of rearrangement observed in reactions 1 - 4 was due to a steric effect, but they were unable to explain this in detail.

Wilt and Philip (10) recently reported other rearrangements in the neophyl system when incorporated into cyclic compounds. The decarbonylation of 1-phenylcyclopentyl- and 1-phenylcyclohexylacetaldehyde gave mixtures of rearranged and unrearranged products. For example, 1-phenylcyclohexylacetaldehyde gave 94% of benzylcyclohexane on decarbonylation at 132° in chlorobenzene. While the extent of rearrangement in both cyclic systems was greater than in the neophyl radical

itself, the 1-phenylcyclohexyl radical rearranged to a substantially greater degree but at a somewhat slower rate than the 1-phenylcyclopentyl radical. The results were interpreted in terms of conformational effects in the various radicals.

Recently, Winstein and co-workers (11) have described a rearrangement in which a homologous neophyl radical rearranged by a 1,4-migration. The decarbonylation of 5-methyl-5-phenylpentanal gave the 4-phenyl-4-methylbutyl radical V which partially rearranged to the 2,2-dimethyl-4-phenylbutyl radical VII as in equation 5a. This is an example of an Ar_1-5 process, of which there are several examples in carbonium ion chemistry (11). A tetralin product VIII was also obtained as a result of an Ar_2-6 rearrangement, equation 5b.



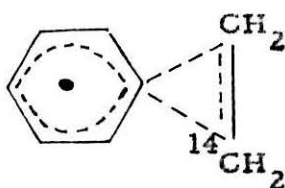
The rearrangement of V to VII is formally analogous to the rearrangement of a neophyl radical. While there is no direct evidence to the contrary, it is unlikely that the bridged radical VI is an intermediate, as

is postulated in the analogous carbonium ion rearrangement. By analogy with Seubold's work (5) on the neophyl radical, it is more probable that VI is a transition state for rearrangement of the primary radical V to the tertiary radical VII.

In the rearrangements of neophyl-type radicals reported above, the phenyl group migrated exclusively - no methyl or hydrogen migration having been observed. The rearrangement always proceeded in a direction which may relieve steric compression of the substituent groups on the carbon atom adjacent to the radical center and also proceeded from an electronically less stable to a more stable radical, usually from a primary to a tertiary radical.

Recently, Slaugh (12) described the rearrangement of the unsubstituted phenylethyl radical, in which case the driving force cannot be due to any of the factors mentioned above. The decarbonylation of 3-phenylpropionaldehyde-2- ^{14}C gave the 2-phenylethyl-1- ^{14}C radical which rearranged to the isomeric 1-phenylethyl-1- ^{14}C radical to the extent of 2.3-5.1% over a temperature range of 140-170°. Since both the rearranged and unrearranged radicals were primary phenylethyl radicals, there was no difference in the stability of the radicals involved in the reaction and, furthermore, there was no steric compression in the phenylethyl radical assisting phenyl migration. The driving force for the rearrangement must be sought elsewhere. Slaugh argued (12) that this rearrangement, as well as those of other radicals containing β -phenyl groups, must be assisted by the delocalization of the odd electron on

the aromatic ring in a structure such as IX which could represent the transition state for the rearrangement, or, in this case, may actually represent an intermediate (see below).



IX

Slaugh's observation that the extent of rearrangement increased with temperature indicates that the activation energy for rearrangement in this case is greater than that for abstraction of a hydrogen atom. In the neophyl case, as discussed earlier, Seubold (5) found that the activation energy for rearrangement was about the same as for hydrogen abstraction, 7-8 kcal/mole, since the extent of rearrangement was not temperature dependent. Slaugh also investigated the possibility of 1,2-hydrogen shifts in the phenylethyl radical by studying the decarbonylation of 3-phenylpropanaldehyde in the presence of benzyl mercaptan-S-t and analyzing the resulting ethyl benzene-t for tritium. He found no evidence for any significant amount of hydrogen migration in this system, just as Curtin and Kauer (9) found no evidence for hydrogen migration in neophyl-type radicals.

Smith and Andersen (13) generated the 2-phenylethyl-1-¹⁴C radical and the 2-phenylpropyl radical from the corresponding bromides

by Kharasch's method (3) and found that the radicals rearranged to the extent of 18.9% and 40%, respectively. Smith and Andersen discussed the greater extent of rearrangement found in these reactions, as compared with that observed in the decarbonylation reaction (12), together with the possibility of the intermediacy of phenyl-bridged radicals, such as IX, in these reactions. On the basis of the available data, the authors could not decide between alternative mechanisms involving "classical" and "non-classical" intermediates in these reactions.

The phenyl-bridged structures III, VI and IX, which are likely transition states (or, less likely, intermediates) in the rearrangements discussed above, are formally analogous to homoallylic radicals in that the interactions postulated (fig. 1) are similar to the 1-2 and 2-4 interactions postulated in homoallylic systems(98,106).



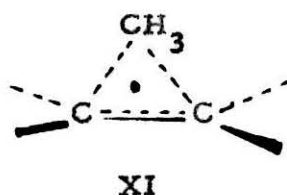
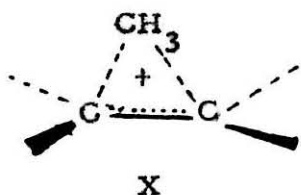
Figure 1

It is predicted on the basis of simple molecular orbital theory that such systems possess substantial delocalization energy. This subject is discussed in detail in a later section (see page 70 ff.).

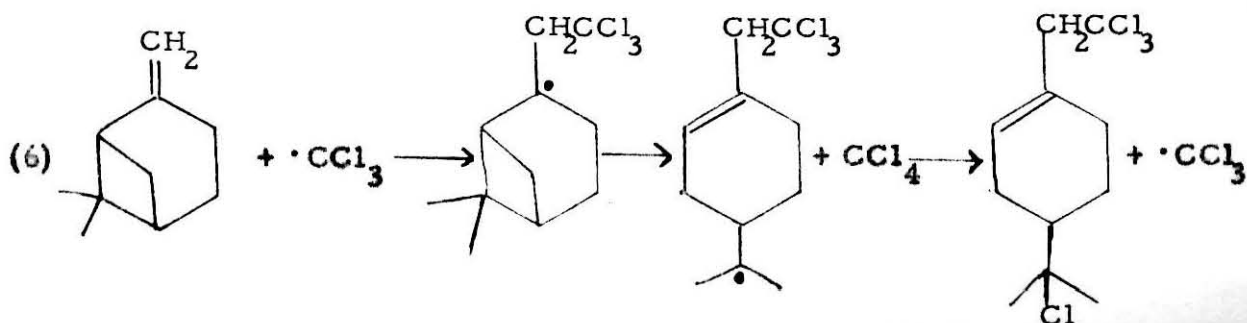
Investigations have been made of radicals related to the neopentyl radical in which there were no phenyl groups on the β -carbon and in which the possibility of alkyl migration was explicitly studied. For example, Seubold (14) found no rearranged products from the decarbonylation of β, β -dimethylvaleraldehyde, cyclopentylacetaldehyde and cyclohexanecarboxaldehyde. In contrast, Kharash, Liu and Nudenberg (15) claim to have observed the 1,2-migration of a methyl group in the bromination of di-t-butylmethane at 200°. The product was supposedly 2-bromo-2,3,4,4-tetramethylpentane. However, as Walling pointed out (16), the method of product identification did not exclude the possibility of a polar rearrangement of the initially formed unrearranged product. Very recently, Backhurst (17) reinvestigated this reaction and confirmed Walling's explanation. No tertiary bromides were formed in the initial bromination reaction and were produced only when the product was treated under the conditions used for product identification by Kharasch and his co-workers (15). Rust and Collamer (18) reported a rearrangement involving the supposed migration of an alkyl group in the reaction of 2,2,4-trimethylpentane with oxygen at 450-470° in which a small amount of 2,5-dimethyl-1-hexene was isolated. However, it is possible and likely that this product arises by recombination of isobutylene and isobutyl radicals which are possible degradation fragments of the first formed radicals; such degradation of radicals at high temperatures is well known (19). Neither one of the above examples of supposed free radical rearrangements involving the 1,2-migration of alkyl groups can

be considered valid or well-authenticated and will not be considered further.

The investigations just discussed suggest that alkyl groups and hydrogen do not undergo 1,2-migrations in free radical reactions while phenyl groups migrate with apparent ease under the same conditions. While "non-classical" bridged carbonium ion intermediates such as X have been postulated as intermediates in many carbonium ion rearrangement reactions (2), the results above indicate that analogous bridged "non-classical" radical structures XI are poor energetically. Theoretical justification for this marked difference between these carbonium ions and free radicals will be given in a later section (see page 64 f.).

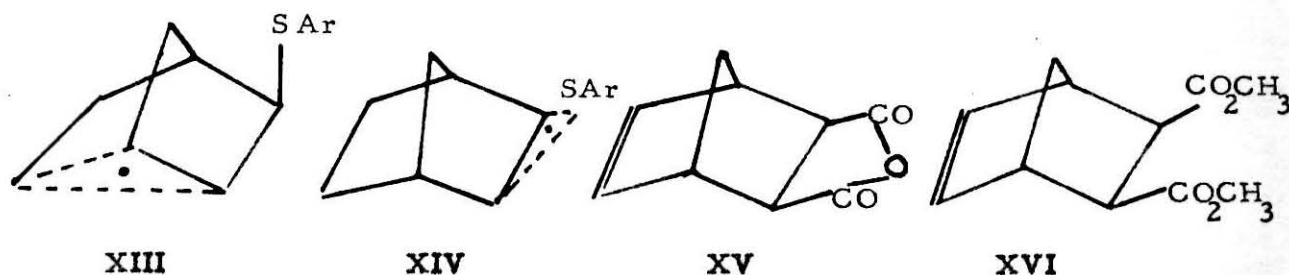


Some free radical rearrangements which do not involve 1,2-shifts have been observed in certain non-aromatic systems. An interesting rearrangement was observed by Oldroyd, Fisher and Goldblatt (20) in the radical addition of carbon tetrachloride to β -pinene. The sole product was XII which appears to arise by the following path:



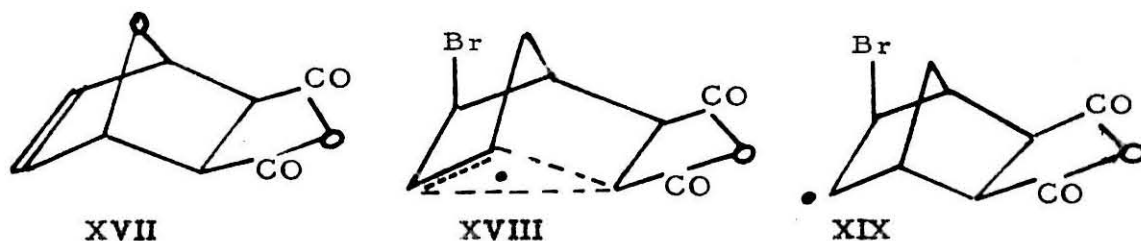
Similar rearrangements have also been observed in the addition of chloroform and ethyl bromoacetate to β -pinene (21). Walling (22) attributes the driving force in these reactions to the relief of strain due to the opening of the four-membered ring present in the starting material. Again, an intermediate structure which is basically homoallylic in character must play a role in this rearrangement.

Cristol and Berson and their respective co-workers have sought for free radical rearrangements in certain bicyclic systems which are prone to extensive rearrangement in carbonium ion reactions. Such a system is the norbornyl (bicyclo [2.2.1] heptyl) system (23). The addition of *p*-thiocresol to norbornylene (24a) gave only unrearranged exo-2-norbornyl *p*-tolyl thioether while the addition of *p*-thiocresol to substituted norbornylenes gave entirely cis-exo addition. In particular, Berson and Jones (24b) observed no rearrangement in the addition of *p*-thiocresol to substituted norbornylenes XV and XVI. These experiments provide evidence against the intermediacy of carbon- and sulfur-bridged radicals such as XIII and XIV, respectively.



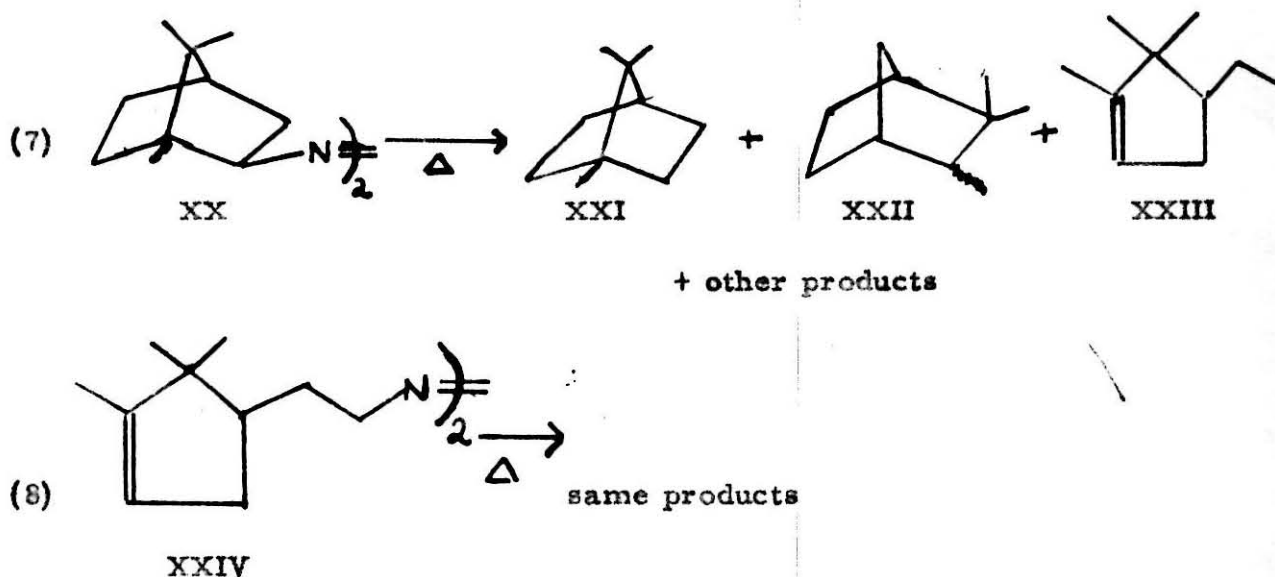
In order to explain the formation of cis-dibromide in addition to trans-dibromide on bromination of XV and the corresponding oxygen-bridged

compound XVII, Berson (25) postulated the intermediacy of a "non-classical" bridged radical XVIII. This interpretation has since been abandoned and the results are now interpreted (26) in terms of a non-



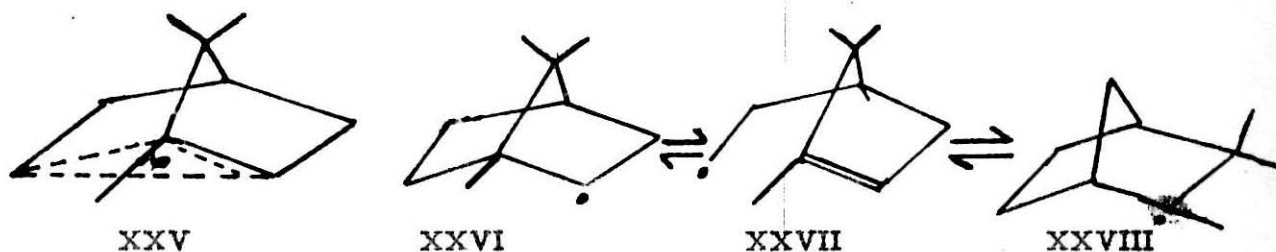
stereospecific attack of bromine on a classical 2-bromonorbornyl radical XIX. Lack of stereospecificity in this particular system is not surprising considering the steric hindrance to reaction of XIX with bromine on both the exo and endo sides of the radical.

In more recent work by Berson (26), the bicyclic radicals were generated by different means than those used in the work described above. Just as Doering obtained no rearranged products from the decarbonylation of 2-formyl-bicyclo[2.2.2]octane (27), Berson (26) found that the decarbonylation of 2-formyl-bicyclo[2.2.1]heptane gave only norbornane while camphane-carboxaldehyde afforded only camphane. The decomposition of azocamphane XX in an inert solvent at 285°, however, gave a mixture of seventeen products (according to vapor-phase chromatography), three of which were camphane XXI, isocamphane XXII, and 2,3,3-trimethyl-4-ethylcyclopentene XXIII. The decomposition of the azo compound XXIV gave a similar mixture (26). The intermediacy of bridged "non-classical" radicals such as XXV in



reactions 7 and 8 seems highly unlikely for the following reasons.

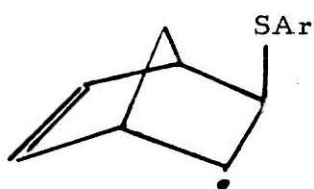
Both the exo and endo isomers of isocamphane are produced. This result



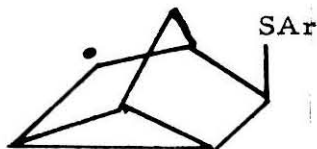
is more in accord with a non-stereospecific attack at an isocamphyl radical XXVIII than with attack on a bridged radical such as XXV which is expected to be stereospecific and to give only the exo isomer. Since fragmentation of radicals occurs readily at such elevated temperatures (285°) (19), it seems more reasonable to explain the results by postulating fragmentation of the camphyl radical XXVI into an open-chain

radical XXVII which can then recyclize to form either a camphyl radical XXVI or an isocamphyl radical XXVIII. While the possibility of 1,2-migration of alkyl groups in these free radicals has not been ruled out definitely, the fragmentation hypothesis seems more likely on the basis of the evidence obtained thus far and by analogy with the other studies reported above. It is also possible that the decomposition of azo compounds produces radicals in an excited state, similar to the "hot" carbonium ions produced by the deamination of amines, and that these radicals may be capable of reactions not possible for "ordinary" radicals. Berson and his co-workers are continuing work on this interesting problem and are now in the process of separating several of the other products by gas chromatography.

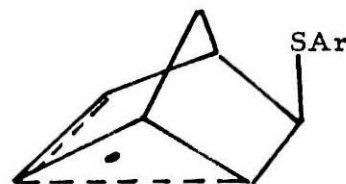
Cristol and his co-workers (28) investigated the addition of *p*-thiocresol to norbornadiene in order to determine whether the products are derived from the isomeric free radicals XXIX and XXX or from the "non-classical" homoallylic radical XXXI. They obtained a mixture



XXIX



XXX



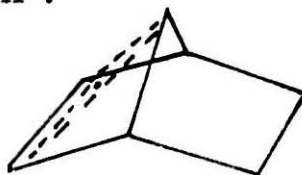
XXXI

of 40% exo-5-norbornen-2-yl *p*-tolyl thioether and 60% 3-nortricyclyl p-tolyl thioether. The ratio of these products was found to be dependent on the thiol concentration indicating that the mixture of products was not

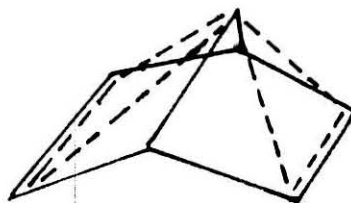
due to attack on the mesomeric "non-classical" radical XXXI at two sites but is more consistent with the intermediacy of two "classical" radicals XXIX and XXX. This result is similar to that obtained by Seubold (5) in the case of the rearrangement of the neophyl radical (see above). In the present case, XXIX was formed first and either rearranged to XXX, most likely through a transition state resembling XXXI, or reacted with thiol in a chain-propagation step. In the absence of isotopic tracer studies, however, it cannot be said with certainty whether more extensive skeletal rearrangement is or is not taking place in this reaction. Considering the general absence of rearrangement involving alkyl group migrations (see above) extensive carbon shuffling in this case seems unlikely.

It is possible, theoretically at least, to have anchimerically assisted processes in which the course of a radical reaction at a particular center in a molecule may be assisted by participation of other groups in the molecule without actually resulting in any net rearrangement. Such a process has been suggested in a recent communication by Story (29). The reaction of norbornadiene with t-butyl ^{benzoate}peroxalate in the presence of cuprous bromide gave 7-t-butoxynorbornadiene. t-Butyl ^{benzoate}peroxalate usually reacts with olefins in the presence of cuprous bromide to give allylic benzoates by a process which has been suggested to be free radical in nature (30). Story (29) suggests that instead of abstraction of an allylic hydrogen at a bridgehead position, abstraction of hydrogen to give a radical at C₇ is assisted by participation of the

π -electrons in a "non-classical" homoallylic structure such as XXXII or XXXIII .



XXXII



XXXIII

The geometry of XXXII and XXXIII are known to be such as to give rise to highly stable "non-classical" homoallylic or bis-homocyclopropenyl carbonium ions (31) and might therefore be expected to give rise to stable types of "non-classical" radical structures. The delocalization energy of XXXIII has been calculated (29) to be 6.7 kcal/mole. The fact that a t-butyl ether was obtained instead of a benzoate raises some doubts as to the free radical nature of this reaction and whether it might not be occurring via a "non-classical" 7-norbornadienyl carbonium ion. Until further data are presented to substantiate Story's hypothesis, the course of this interesting reaction must be considered to be still in doubt.

Aside from studies on the behavior of radicals in simple small-ring systems, to be discussed in detail below, the investigations reported above virtually cover the field of free radical rearrangements. In comparison with carbonium ion rearrangements, it can be seen that the number of free radical rearrangements is meager. Many systems which rearrange in carbonium ion reactions fail to do so in free radical reactions. The only well documented examples of 1,2-migrations in

free radicals involve phenyl migrations, although the possibility of migration of alkyl groups has been rather carefully looked for. The larger amount of rearrangements in neophyl-type radicals as compared to phenylethyl radicals suggests that relief of steric compression at the β -carbon and the formation of a tertiary radical on rearrangement lowers the activation energy for rearrangement. However, the latter two effects alone are insufficient to promote rearrangement in other systems as can be deduced from the total lack of rearrangement of primary radicals related to the neopentyl radical which are also sterically compressed at the β -carbon atom.

Authenticated cases of rearrangement of carbanions are fewer even than the cases of free radical rearrangements. The types of rearrangement which have been observed are related to those found previously in free radical chemistry. 1,2-Migration of a phenyl group in a carbanion related to a neophyl carbanion has been reported very recently by Zimmerman and Zweig (32). They found that 2,2-diphenylpropyllithium, which is stable in ether at 0°, rearranged in refluxing solvent to 1,2-diphenylethyllithium. An investigation of the unsubstituted phenylethyl system in a carbanion reaction has recently been carried out in these laboratories (33). Phenylethylmagnesium bromide was prepared from 2-phenylethyl-1-¹⁴C bromide and the extent of shuffling of the isotopic label from the products of oxygenation was determined to be 0.2-0.3% at the very most after 48 hrs. This result is to be compared with 2-20% rearrangement of the phenylethyl radical (12,13) and up to

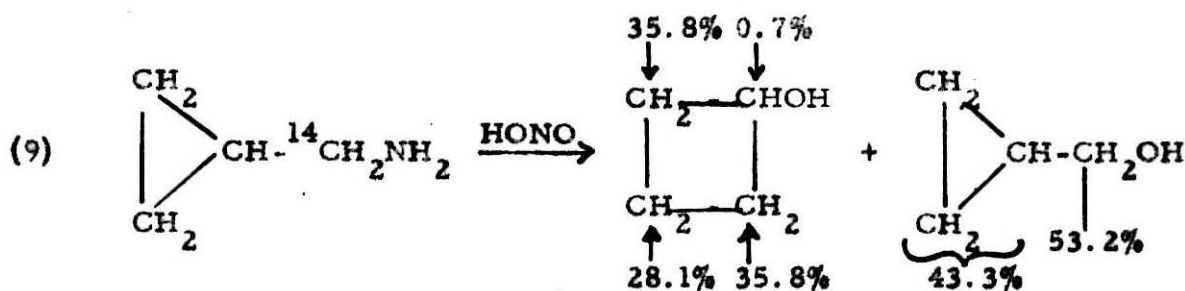
50% rearrangement of the phenylethyl carbonium ion (34). No cases of the 1,2-migration of a saturated alkyl group are known. A case of a 1,2-migration of a vinyl group has recently been discovered (35) and will be discussed below in connection with rearrangements in small-ring systems. These few examples cover the entire field of carbanion rearrangements. A theoretical argument will be given later to suggest why few examples of carbanion rearrangements have been observed and probably will be observed.

Carbonium Ion and Carbanion Rearrangements in Small-Ring Systems

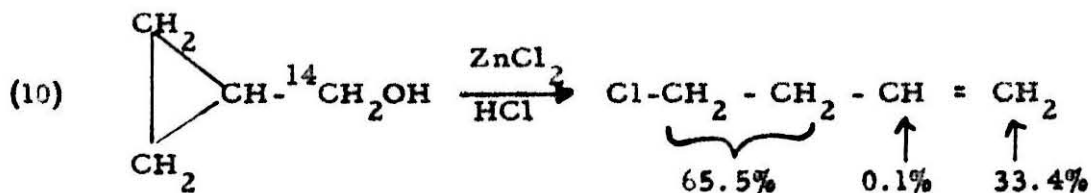
In the discussion of free radical rearrangements given above, the area of small-ring systems has purposely been omitted. Since this thesis specifically concerns the reactions and rearrangements of small-ring radicals, a detailed discussion is given below of the evidence which has been obtained prior to this work on the behavior of these particular free radicals. In order to put the problem into proper perspective with respect to the general discussion of rearrangements given above, a brief summary is given below of the extensive work which has been done on carbonium ion and, to a lesser extent, carbanion rearrangements in small-ring systems.

The solvolysis of cyclopropylcarbinyl and cyclobutyl halides and sulfonate esters, the reaction of cyclopropylcarbinol with thionyl chloride, hydrogen bromide and phosphorous tribromide, and the deamination of cyclopropylcarbinylamine and cyclobutylamine are all reactions which

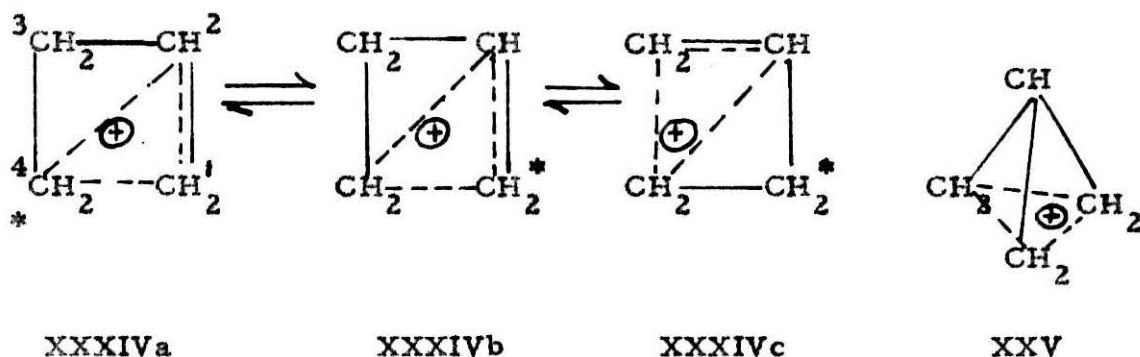
proceed with extensive rearrangement and which are postulated to occur via "non-classical" cationic intermediates (36). These reactions all give mixtures having closely similar relative amounts of products with cyclopropylcarbinyl, cyclobutyl and allylcarbinyl structures. For example, the same mixture of 47% cyclopropylcarbinol, 48% cyclobutanol and 5% allylcarbinol is obtained on deamination of either cyclopropylcarbinylamine or cyclobutylamine. Studies of the products of the deamination of cyclopropylcarbinylamine- α - ^{14}C showed that extensive internal rearrangement occurs in this reaction, as shown by the ^{14}C distribution given in equation 9.



The above reaction is an example of an irreversible carbonium ion reaction. In contrast, the reaction of cyclopropylcarbinol with Lucas reagent is an example of a reversible carbonium ion reaction and the only product isolated is allylcarbinyl chloride. The product in the latter reaction is said to be due to equilibrium control of the reaction while the products of deamination of amines are products of a kinetically-controlled reaction. Thus, with isotopically labeled cyclopropylcarbinol, equation 10, the ^{14}C -label was equally distributed between the three methylene groups of the product.



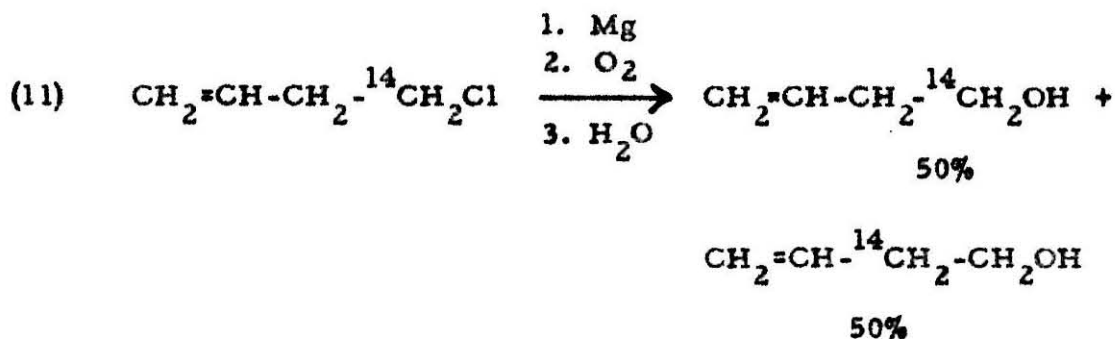
These rearrangements, and many other related ones, can be explained on the basis of equilibrating classical cations. The abnormally large solvolytic reactivity of cyclopropylcarbinyl and cyclobutyl derivatives, however, cannot be explained on the basis of simple cationic intermediates and this, together with the rearrangement data, has led to the suggestion that bridged "non-classical" carbonium ion intermediates are involved. The most recent data are best explained on the basis of rapid equilibration of three unsymmetrical bicyclobutonium ions, XXXIVa-c, in which the asterisk represents an isotopic label so as to distinguish between the three species.



In the bicyclobutonium ion, a specific 1,4-interaction is included along with the 1,2- and 2,4-interactions which are characteristic of "non-classical" homoallylic carbonium ions. This 1,4-interaction is postulated to account for the formation of cyclobutyl derivatives from allylcarbinyl and cyclopropylcarbinyl derivatives, and vice versa. The

tricyclobutonium ion XXXV, which was at one time considered to be an intermediate in these reactions (37), is now considered to be no more than a likely transition state for interconversion of the three bicyclobutonium ions (1).

The behavior of cyclopropylcarbinyl, cyclobutyl and allylcarbinyl derivatives in carbanion reactions is markedly different. Cyclobutyl halides form Grignard reagents which react normally to give unrearranged products (38). However, cyclopropylcarbinyl halides form Grignard reagents which react to give allylcarbinyl products exclusively (38). While the allylcarbinyl Grignard reagent gives only open-chain products, it was recently observed (35) that the Grignard reagent prepared from 1-chloro-3-butene-1-¹⁴C (isotopically labeled allylcarbinyl chloride) gave equal amounts of rearranged and unrearranged products on oxygenation some 24 hours after formation, as in equation 11.

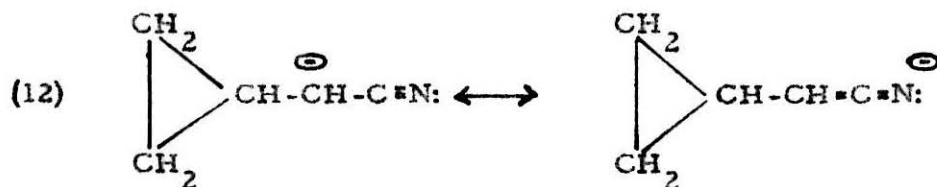


An n-m-r study of the rearrangement of 1,1-dideutero-3-butenylmagnesium bromide to 2,2-dideutero-3-butenylmagnesium bromide and of the products of oxygenation and carbonation has shown that the Grignard reagent rearranged after its formation and prior to conversion to final products.

These results, which may be described as involving a 1,2-migration of a vinyl group, are consistent with the intervention of a cyclopropylcarbinyl carbanion structure, either as an intermediate or a transition state, somewhere between formation of the allylcarbinyl Grignard reagent and the formation of products. This interconversion of cyclopropylcarbinyl and allylcarbinyl structures appears to be fundamentally different from that involved in the carbonium ion rearrangements. First, only allylcarbinyl derivatives, corresponding to the product of equilibrium control, are isolated from these Grignard reactions. Second, the completely normal reactions of the cyclobutyl Grignard reagent indicate that cyclobutyl intermediates are not involved in the interconversion of cyclopropylcarbinyl and allylcarbinyl structures. Consequently, it seems reasonable to believe that no intermediates are involved which, like the bicyclobutonium cations, have substantial cyclobutyl character. This idea will be supported later by a theoretical argument (see page 64 ff.). It can be noted here that there are no similar theoretical objections to "non-classical" homoallylic carbanion intermediates in these reactions, although available evidence does not as yet demand that such intermediates be invoked to explain the course of the reactions.

Evidence has been obtained in the course of synthetic work described in this thesis (see page 138) that not all varieties of cyclopropylcarbinyl carbanions react with ring opening. Thus, the reaction of cyclopropylcarbinyl cyanide with sodamide and methyl bromide in

liquid ammonia gave only dimethylcyclopropylcarbinyl cyanide. Apparently, the cyano group stabilizes the carbanion by resonance, as in (12) and dominates over the effect of the neighboring cyclopropyl group



so as to lead exclusively to the formation of unrearranged products.

Studies are now being made (39) of the reaction of various substituted allylcarbinyl Grignard reagents in the hope of isolating cyclic compounds from these reactions also.

Free Radicals in Small-Ring Systems

It might have been anticipated on the basis of the discussions above that rearrangement of cyclopropylcarbinyl free radicals would occur. Such rearrangements have indeed been found.

In order to determine the scope of these rearrangements and perhaps the nature of the intermediate radicals involved relative to those in the corresponding carbonium ion and carbanion rearrangements, the reactions of a number of small-ring radicals have been studied in the course of this work. The following discussion summarizes evidence available from earlier work on the reactions and behavior of small-ring radicals.

Most of the literature concerning the formation and reactions of cyclopropyl and cyclopropylcarbinyl free radicals is summarized in the

recent paper of Hart and Wyman (40) and will be discussed only briefly here, together with the available evidence concerning cyclobutyl radicals.

Cyclopropyl radicals have been generated under a variety of conditions. The products of photochemical chlorination (41) and vapor-phase nitration (42) of cyclopropane and brominative decarboxylation of silver cyclopropanecarboxylate (43a) all have cyclic structures. Applequist and Peterson (44) recently found that the same mixture of cis and trans 2-methylcyclopropyl bromide was obtained from the Hunsdiecker reaction of either cis or trans silver 2-methylcyclopropanecarboxylate. This result implies that the 2-methylcyclopropyl radical is either planar or is rapidly inverting its configuration (see page 62 for further discussion of this subject). Open-chain products are formed in the Kolbe electrolysis of potassium cyclopropanecarboxylate (45), in the thermal chlorination of cyclopropane (41) and in the photolysis of methyl cyclopropyl ketone (46). Whether the products isolated from cyclopropyl radicals are unrearranged or are derived from allyl radicals seems to be mainly determined by the reaction temperature. At low temperatures, the cyclopropyl radical is stable, while at high temperatures (above 200°) it isomerizes to the allyl radical from which the products are derived (see page 62). The ring opening which occurs in the photolysis of methyl cyclopropyl ketone (46) appears to be an exception to this generalization. Cyclopropyl radicals, as such, do not appear to be intermediates, since other primary processes appear to be involved which

afford ring opening directly.

It is relatively difficult to generate cyclopropyl radicals under mild conditions. Hammond and Todd (47) observed no tendency for hydrogen abstraction when cyclopropanecarbonitrile, methyl cyclopropyl ketone and phenylcyclopropane were treated with typical radical chain initiators. Trotman-Dickenson and Steacie (48) found it more difficult to remove a hydrogen atom from cyclopropane than from hydrocarbons such as n-butane, propylene, 1-butene, cyclobutane, benzene and toluene, when these substrates were treated with methyl radicals generated by acetone photolysis. By studying the reaction of trideuteromethyl radicals with a mixture of cyclopropane and cyclopentane at 250-400°, McNesby and Gordon (49) were able to show that the activation energy for abstraction of hydrogen atoms from these substrates was 13.1 and 9.3 kcal/mole, respectively. The products isolated, derived from cyclopropane, had the allyl structure. The reluctance and difficulty with which cyclopropyl radicals are formed resembles the lack of solvolytic reactivity of cyclopropyl derivatives (43b) and is discussed in detail in a later section (see page 57 ff.).

Vapor-phase chlorination of cyclobutane gave only cyclobutyl chloride (38). The photolysis of methyl cyclobutyl ketone from 60-250° (50) afforded products with the cyclobutane ring intact as well as same products derived from fragmentation of the cyclobutyl radical, but no simple ring-opened products. The reaction of bromine and silver cyclobutanecarboxylate (51) gave exclusively cyclobutyl bromide. This

last result is significant in another respect - namely, the failure to observe any rearranged products argues against the intermediacy of carbonium ions in this reaction and is good evidence for the free radical nature of the Hunsdiecker reaction. Abstraction of a hydrogen atom from cyclobutane takes place more easily than from cyclopropane, but still with a higher activation energy than from cyclopentane, according to the results of Trotman-Dickenson and Steacie (48).

These scattered investigations show that cyclobutyl radicals can be formed without difficulty, and maintain their cyclic identity at temperatures up to 250°. It has recently been reported (52) that cyclobutyl radicals open at temperatures above 250° to give butenyl radicals which afford olefinic products.

The radical of particular interest in this work is the cyclopropylcarbinyl radical. Previously, Roberts and Mazur (38) reported that the photochlorination of methylcyclopropane gave a complex mixture of chlorides containing 21% ring-chlorinated material, 35% allylcarbinyl chloride, 34% cyclopropylcarbinyl chloride and 10% of intermediate fractions. Product identifications were based on infrared analysis. Brown and Borkowski (53) repeated the same reaction at -20° and the only product that they identified was cyclopropylcarbinyl chloride, which was the major low-boiling product. Subsequent analysis (54) of some of the low-boiling distillation fractions whose analyses were not reported by Brown and Borkowski (53) indeed showed the presence of allylcarbinyl chloride in addition to cyclopropylcarbinyl chloride. Photochlorination

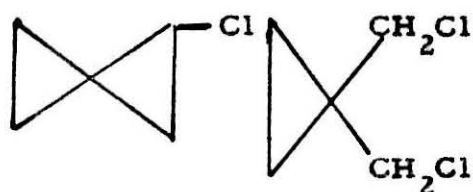
of dicyclopropylmethane at -80° (55) gave only 1-cyclopropyl-4-chloro-1-butene and hence proceeded exclusively with ring opening.

The chlorination of methylcyclopropane was recently reinvestigated in these laboratories by Dr. E. Renk (56). The products were analyzed by vapor-phase-chromatography (v-p-c). As before, the product mixtures were found to be exceedingly complex, composed of as many as twenty different components. Cyclopropylcarbinyl chloride and allylcarbinyl chloride were identified as the main mono-chlorinated products. Pure samples of each of these chlorides were obtained on separation by v-p-c using a preparative column. The ratio of these chlorides varied from 16:1 to 1:2 (cyclopropylcarbinyl:allylcarbinyl chlorides) as the chlorine flow-rate and the extent of reaction were varied. In experiments in which almost all the methylcyclopropane was consumed, relatively little allylcarbinyl chloride was found, but relatively large amounts of a higher-boiling component were present, according to the vapor-phase-chromatogram. It is presumed that this component is 1,2,4-trichlorobutane, formed by the addition of chlorine to the double bond of allylcarbinyl chloride. In experiments in which the reaction was interrupted while there was still excess methylcyclopropane, large quantities of allylcarbinyl chloride were obtained relative to cyclopropylcarbinyl chloride (in ratios up to 2:1) and only small amounts of the higher-boiling component were present. These experiments show that allylcarbinyl chloride is consumed by excess chlorine while cyclopropylcarbinyl chloride is consumed relatively slowly. No

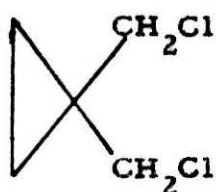
cyclobutyl chloride could be detected, although 1-methyl-1-chlorocyclopropane and 1-methyl-2-chlorocyclopropane were found to be present. None of the many higher-boiling polychlorinated products were identified.

Renk (56) also studied the photochlorination of methylcyclopropane- α - ^{13}C . Allylcarbinyl chloride and cyclopropylcarbinyl chloride (ratio 2:1) were separated from the other components in the reaction mixture by means of v-p-c, using a preparative column. Each of these chlorides was analyzed by nuclear magnetic resonance (n-m-r) and the ^{13}C -distribution was determined with an uncertainty of no greater than $\pm 10\%$. It was found that cyclopropylcarbinyl chloride was formed without rearrangement; all the excess ^{13}C was located in the α -position. Similarly, allylcarbinyl chloride was formed with all the excess ^{13}C in the olefinic methylene group. Apparently, ring opening to give allylcarbinyl chloride occurs without measurable scrambling of the carbon atoms.

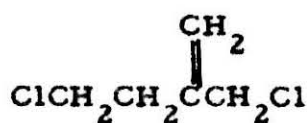
Applequist, Fanta and Henrikson (57) recently studied the chlorination of spiropentane under various conditions, a reaction in which both cyclopropyl- and cyclopropylcarbinyl-type radicals are presumed to be involved. Four products were obtained from the photochlorination, thermal chlorination and liquid-phase chlorination of spiropentane. These were identified as chlorospiropentane XXXVI, 1,1-bis-(chloromethyl)-cyclopropane XXXVII, and open-chain chlorides XXXVIII and XXXIX. The relative amounts of these chlorides changed according to the reaction conditions. The yield of chlorospiropentane XXXVI decreased as the temperature was lowered, indicating that the



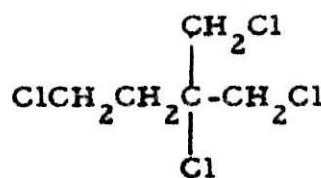
XXXVI



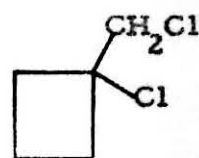
XXXVII



XXXVIII

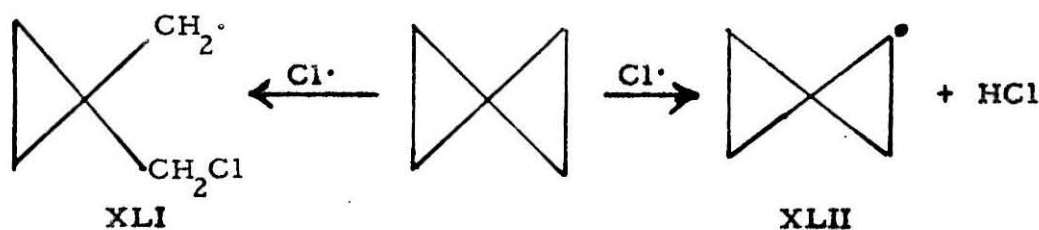


XXXIX

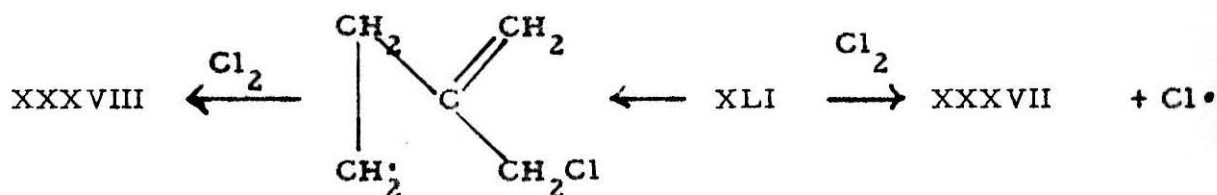


XL

activation energy for hydrogen abstraction to give a cyclopropyl-type radical XLII is greater than the energy for formation of a cyclopropyl-carbinyl-type radical XLI by essentially a radical displacement on spiro-pentane by chlorine.

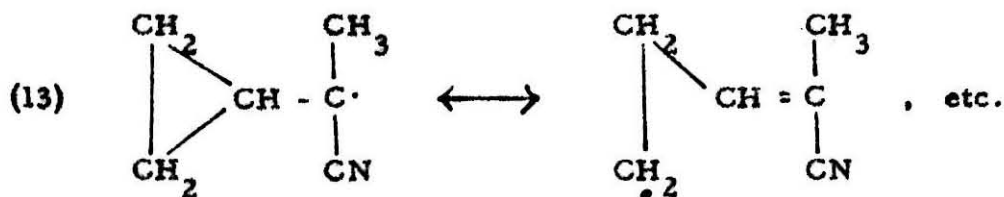


The cyclopropylcarbinyl-type radical XLI reacts both with and without ring opening, as was found by Roberts and Mazur (38) and by Renk (56) in the case of the simple cyclopropylcarbinyl radical as generated in the chlorination of methylcyclopropane.

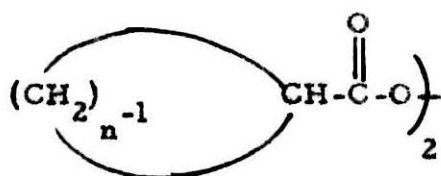


It is interesting to note that, in Applequist's experiments, the formation of XXXVII seems to be favored over XXXVIII as the temperature is lowered. The product XXXIX is formed by addition of chlorine to the double bond of XXXVIII. This supports Renk's hypothesis (56) that the small yield of allylcarbinyl chloride from the photochlorination of methylcyclopropane in the presence of excess chlorine is due to addition of chlorine to the double bond to give polychlorinated products. A small yield of XL is found among the products of the chlorination of spiro-pentane and probably arises wholly or in part from methylenecyclobutane which was known to contaminate the spiro-pentane.

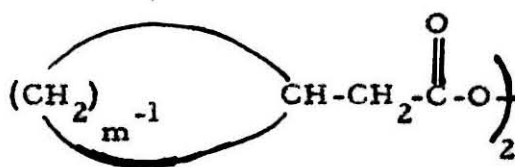
Overberger and Lebovits (58) have studied the decomposition of a number of azo-bis-nitriles derived from the corresponding methyl alkyl ketones. They found that the azo-bis-nitrile derived from methyl cyclopropyl ketone decomposed appreciably faster than any other of a series of azo nitriles derived from ketones including other methyl cycloalkyl ketones. Unfortunately, they did not examine the products of these reactions. Overberger and Lebovits postulated that this accelerated rate was due to stabilization of the cyclopropylcarbinyl radical intermediate by resonance of the following type:



Because of the complications inherent in the photochlorination experiments, due to concurrent formation in primary processes of other radicals besides the cyclopropylcarbinyl radical, it was desirable to study this and other small-ring radicals as generated by a reaction in which only the desired radical would be formed. Its subsequent behavior could then be followed more clearly. Hart and Wyman (40) recently studied the properties of some of these radicals as generated by the decomposition of diacyl peroxides XLIII and XLIV, derived from cycloalkanecarboxylic acids and cycloalkaneacetic acids, respectively.



XLIII



XLIV

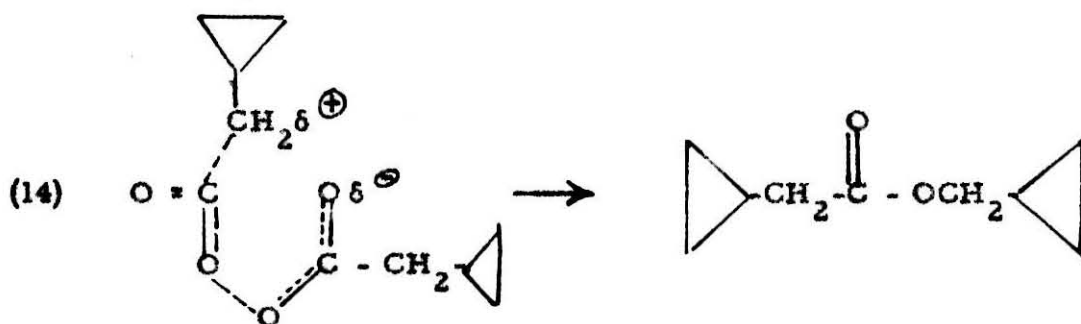
In the decomposition of the peroxides XLIII in carbon tetrachloride, the relative rates for ring sizes from 3 to 7 were 0.44: 7.4: 31.7: 60.3: 71.0, respectively. The spread involves a factor of greater than 10^2 . The decreased reactivity of cyclopropanecarboxylic acid peroxide is in accord with the earlier evidence regarding the difficulty of formation of cyclopropyl radicals. The fact that the stability (or instability) of the resulting radicals is reflected in the rate of decomposition of the peroxides is in agreement with studies of the decomposition of a series of *t*-butyl peresters, $\text{RCOOO-}t\text{-Bu}$, by Bartlett and Hiatt (59). As R was varied, the rate of decomposition of the perester increased as the

stability of $R\cdot$ increased, implying considerable $R-C$ as well as $O-O$ bond breaking in the transition state of the reactions; this same effect is shown in the series of peroxides studied by Hart and Wyman (40). The reaction products were carefully examined and it was determined that no rearrangements of small-ring radicals had occurred. Cyclopropanecarboxylic acid peroxide at 70° gave cyclopropyl chloride as the main product, along with smaller amounts of cyclopropanecarboxylic acid and cyclopropyl cyclopropanecarboxylate. Allyl chloride was sought for but was not found. The lack of ring opening at these temperatures is in accord with the generalizations on the stability of cyclopropyl and cyclobutyl radicals made earlier.

The rate of decomposition of the series of cycloalkaneacetyl peroxide in carbon tetrachloride showed little variation as the ring size was varied from 4 to 6. The rates were slower than those of the peroxides XLIII, ring size 4 to 7, and were about the same as the rates of decomposition of acetyl, propionyl and n-butyryl peroxides. The products were as expected, the main product in each case being the corresponding cycloalkylcarbinyl chloride.

The behavior of cyclopropaneacetyl peroxide (XXIV, $m = 3$) was very erratic. The rate of its decomposition varied from sample to sample by a factor of more than 600. The relative rates, compared to a value of about 2 for the other peroxides, $m = 4$ to 6, varied from 23 to 1200. While it is tempting to regard these results as evidence

of highly stabilized cyclopropylcarbinyl radicals, the nature of the product shows that this is probably the wrong interpretation. No cyclopropylcarbinyl chloride was isolated; the main product was the ester, cyclopropylcarbinyl cyclopropylacetate. A cyclic transition state involving appreciable carbonium ion character at the carbinyl carbon atom has been postulated by Hart and Wyman (40) to explain the formation of ester, as in equation 14.



However, ester formation from peroxides may also occur by an S_N1 mechanism involving ion-pair intermediates, as in the formation of esters by the decomposition of nitrosoamides (60), and such a mechanism does not require a cyclic transition state. Indeed, there is substantial evidence from studies of nitrosoamide decompositions to show that a cyclic transition state is not involved (61), and by analogy, the same may be true of the formation of esters from peroxides. At any event, the increased rate noticed in the decomposition of cyclopropane-acetyl peroxide (40) is probably due to a fast polar reaction which competes very well with the relatively slow free radical reaction. The great stability of carbonium ions derived from cyclopropylcarbinyl derivatives (1) makes such an interpretation seem quite plausible. A recent

communication from Prof. Hart substantiates these considerations. Carefully purified cyclopropaneacetyl peroxide decomposes much more slowly than was found in the earlier work, probably exclusively by a free radical path. The exact rate of decomposition and the nature of the products of the free radical reaction have not as yet been reported.

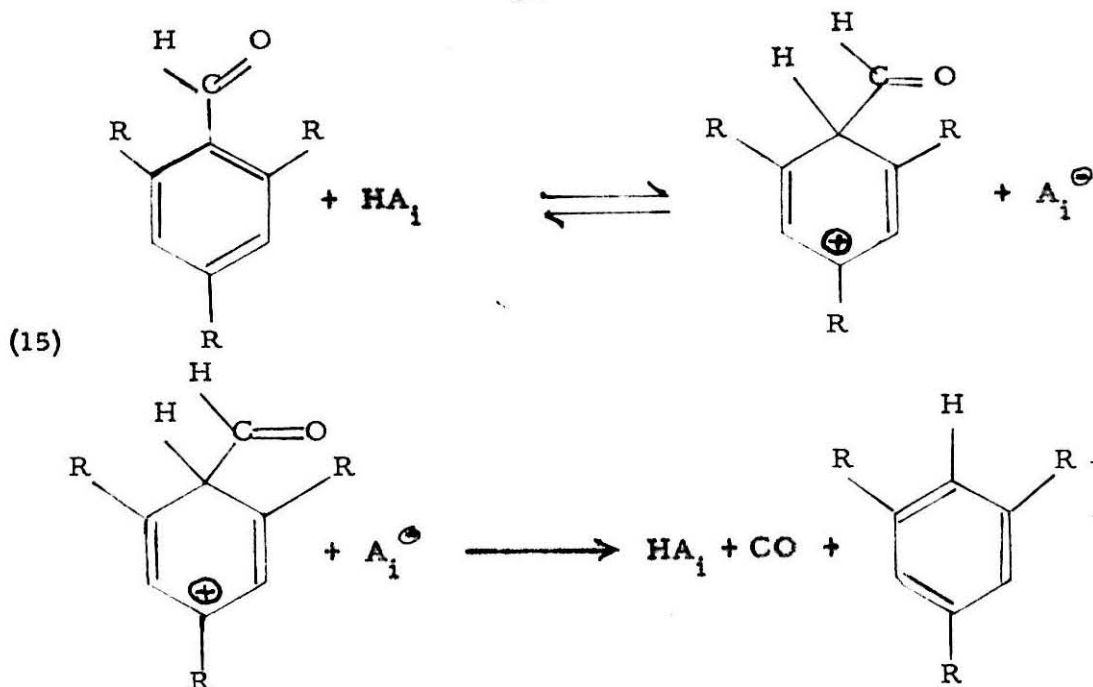
In experiments designed for the generation and study of the cyclopropylcarbiny radical, Urry and Hartzler (63) studied the peroxide-initiated decarbonylation of cyclopropylacetaldehyde. In these unpublished experiments, the aldehyde used was quite impure, as judged by comparison of its physical properties with samples prepared in the present work. A more complete discussion will be given later (see page 130). Urry and Hartzler (63) determined that the exclusive decarbonylation product was 1-butene and this result has now been confirmed in this study.

From the experiments described above, it is apparent that cyclopropylcarbiny radicals rearrange at moderate temperatures. In some studies, mixtures of cyclic and olefinic products were obtained while in others only open-chain products were isolated. The latter result is reminiscent of the rearrangements which occur with the Grignard reagents prepared from cyclopropylcarbiny halides (see above). In the course of the work now to be described, rearrangements involving the cyclopropylcarbiny radical have been studied with the hope of determining the nature of the interesting radical intermediate(s) involved. A number of other small-ring radicals were prepared under similar

conditions and the amount and nature of rearranged and unrearranged products has been determined in each case.

The desired radicals were prepared by decarbonylation of the corresponding cycloalkanecarboxaldehydes and cycloalkylacetaldehydes. This method of generating radicals offers several advantages. The free radical decarbonylation produces radicals of known structure at the carbon atom adjacent to the formyl group without the simultaneous formation of radicals at other centers in the molecule; the progress of the reaction can be easily followed by measuring the amount and rate of carbon monoxide evolution; the products of the chain reaction are hydrocarbons which, in most cases, are easily separated from the other components of the reaction mixture and which can be conveniently analyzed by gas chromatographic and spectroscopic methods. These advantages have been recognized by other investigators in the field of free-radical rearrangements (4, 5, 8, 9, 10, 11, 12, 14, 27) and are discussed in particular by Walling (64).

While the free-radical mode of decarbonylation seems to be general for all aldehydes, decomposition by a polar mechanism has been noted in aldehydes containing certain structural features. 2,4,6-Trialkylbenzaldehydes are known to undergo decarbonylation in strong mineral acid (65) to give hydrocarbons (electrophilic substitution by hydrogen) according to the following mechanism:



Polar decarbonylation of aliphatic aldehydes is not known, and it can be seen by examination of the above mechanism that if saturated aldehydes were to undergo polar decarbonylation, they would have to do so by a very different mechanism than that postulated for substituted benzaldehydes. It is known that formic acid, benzoylformic acid, α -hydroxy acids and acids in which a tertiary alkyl group is bonded to the carboxyl group undergo decarbonylation in strong acid (66). In all of these examples of decarbonylation in strong acid solution, a stable carbonium ion is formed. It is possible that there may be a polar mechanism for decomposition of aldehydes in general of type RCHO where R^+ is a stable carbonium ion although such reactions are not yet known. It is therefore assumed at this time that the decarbonylation of aliphatic aldehydes under non-acidic conditions occurs only by a radical mechanism. It is, of course, possible that the aldehydes are oxidized to acids

which then undergo polar decomposition, but this seems unlikely under the reaction conditions. The decarbonylation of aldehydes therefore seems superior to the decomposition of peroxides as a method of generating radicals since peroxides often undergo polar as well as radical decompositions (67) and it is sometimes very difficult to eliminate the polar reaction in order to study only the radical reaction. This difficulty is well illustrated by the work of Hart and Wyman (40) in which the radical decomposition of cyclopropaneacetyl peroxide was obscured by a polar reaction which they were only able to eliminate, although perhaps not completely, by scrupulous purification of the peroxide.

II. RESULTS AND DISCUSSION

Synthetic Methods

Cyclopropanecarboxaldehyde, 1-methylcyclopropanecarboxaldehyde and 1-phenylcyclopropanecarboxaldehyde were prepared by reduction of the corresponding nitriles with lithium aluminum hydride in yields of 47%, 77% and 57%, respectively. The procedure was based on Smith and Rogier's synthesis of cyclopropanecarboxaldehyde from cyclopropanecarbonitrile (68) and was modified slightly in the case of the substituted compounds. The nitriles were prepared by established procedures (see Experimental). 1-Methyl- and 1-phenylcyclopropanecarboxaldehyde are new compounds whose structures were assigned on the basis of their infrared and n-m-r spectra, elemental analysis, the preparation of derivatives and the method of synthesis. The synthesis of aldehydes by reduction of nitriles through inverse addition of lithium aluminum hydride at low temperatures is apparently general for aldehydes in which the alpha position is either trisubstituted or the hydrogens thereon are unactivated. Yields are generally good (50-80%), and the product can usually be obtained directly in fairly pure form. The main impurities are unreacted nitrile and amine; the latter is obtained by complete reduction of the nitrile. Separation of the aldehyde from the nitrile may be achieved by fractional distillation while the amine is conveniently

removed by extraction with mineral acids and can be isolated if desired. (1-Phenylcyclopropyl)-carbinylamine was isolated in a yield of 9.2% as a by-product in the synthesis of 1-phenylcyclopropanecarboxaldehyde. There was also obtained a high-boiling neutral compound which gave the same 2,4-dinitrophenylhydrazone as 1-phenylcyclopropanecarboxaldehyde. On the basis of this information, together with spectral and analytical data, the compound was assigned the structure of the Schiff's base of 1-phenylcyclopropanecarboxaldehyde and (1-phenylcyclopropyl)-carbinylamine.

Several other methods of synthesis of cyclopropanecarboxaldehyde were investigated, but were found to be inferior to the reduction of the nitrile. The dehydrogenation of cyclopropylcarbinol over copper-zinc at 300° and the oxidation of cyclopropylcarbinol by the Oppenauer method and with chromic acid, manganese dioxide and potassium persulfate all afforded mixtures of cyclopropanecarboxaldehyde and recovered cyclopropylcarbinol; separation by fractional distillation was unsuccessful. Analysis by v-p-c indicated that the yields of aldehyde were not high enough to warrant investigation of other separation methods. The recently reported syntheses of aldehydes by reduction of the corresponding acid chlorides (69) and N,N-dimethylamides (70) with lithium tri-t-butoxy- and diethoxyaluminumhydrides, respectively, were also studied.* Isotbutyl derivatives, used as model compounds, were studied in addition

*In a communication received from Prof. Brown prior to the publication of this synthesis (71), the use of lithium triethoxyaluminumhydride was described. The trisubstituted hydride was used in all our experiments.

to the cyclopropane compounds. Derivatives of the respective aldehydes were obtained in satisfactory yield when the reaction mixtures, after hydrolysis, were treated directly with 2,4-dinitrophenylhydrazine reagent. However, isolation of the aldehydes from reaction mixtures containing ethyl or *t*-butyl alcohol proved to be difficult. Attempts at separation of the aldehydes in satisfactory yield by fractional distillation and by regeneration from derivatives were unsuccessful.*

Several routes were investigated for the synthesis of cyclopropylacetaldehyde. The newly reported synthesis of cyclopropane compounds by the reaction of olefins, methylene iodide and zinc-copper couple (Simmons-Smith (72)) seemed to be a convenient way to prepare cyclopropane compounds which might be convertible by simple manipulation of functional groups into cyclopropylacetaldehyde.** The experimental procedure was tested with cyclohexene and styrene which were found to be converted into bicyclo[4.1.0]heptane and phenylcyclopropane, respectively. Allyl cyanide, allylcarbinol and allylcarbonyl acetate were

*These results suggest that Brown's methods of synthesis of aldehydes (69, 70) may not be applicable to the cases of low-boiling water-soluble aldehydes in cases where isolation of the aldehyde and not an aldehyde derivative is desired.

**Most of the olefins subjected by Simmons and Smith (72) to this reaction were hydrocarbons which were converted to the corresponding cyclopropane compounds in yields of 45-70%. Lower yields were obtained in the cases of the few compounds studied containing additional functional groups. The scope of the reaction with respect to the range of functional groups possible in olefins subjected to the Simmons-Smith reaction has yet to be determined.

prepared and subjected to this reaction. Allyl cyanide only afforded tars; allylcarbinol was apparently unreactive as 70% was recovered from the reaction mixture; allylcarbinyl acetate gave some 2-cyclopropylethyl acetate in addition to recovered olefin. The cyclic ester was separated by treatment of the mixture with alkaline permanganate solution and the pure product, identified by its spectral properties, was isolated in an overall yield of 8.3%. Unsuccessful attempts were made to convert 3-butenal dimethyl and diethyl acetals directly to cyclopropylacetaldehyde dimethyl and diethyl acetals. The starting acetals were gradually consumed under Simmons-Smith conditions but complex mixtures resulted, from which no identifiable products could be isolated. The same result was obtained with 3-methyl-3-butenal dimethyl and diethyl acetals. Control experiments with cyclohexene showed that the reagents were active and that the negative results were due to side reactions with the acetals as substrates. The open-chain acetals were prepared by the reaction of methyl and ethyl orthoformate with Grignard reagents prepared from allyl bromide and methallyl chloride. These reactions invariably gave mixtures of product and recovered ortho ester. In one run, both Grignard reagent and ortho ester were shown to be present after the mixture had been stirred at reflux for five days. 3-Butenal dimethyl and diethyl acetals could not be isolated in pure form by fractional distillation, but the 3-methyl homologs were obtained in a pure state and were characterized by their infrared and n-m-r spectra and elemental analysis.

The preparation of 2-cyclopropylethanol was investigated with the intention of oxidizing it to the desired cyclopropylacetaldehyde. Hart (73) reported that 2-cyclopropylethanol could be prepared by the reaction of ethylene oxide with cyclopropylmagnesium chloride, prepared from cyclopropyl chloride in tetrahydrofuran. In our hands, an alcohol was obtained which was originally thought to be 2-cyclopropylethanol but was later shown to be ethylene chlorohydrin. Authentic 2-cyclopropylethanol was prepared by the reduction of methyl cyclopropylacetate with lithium aluminum hydride in a crude yield of 52% and was characterized by its infrared and n-m-r spectra, the preparation of a 3,5-dinitrobenzoate, and agreement of its physical properties with those reported for the alcohol as prepared alternatively by Hart and Wyman (40) via cyclopropyllithium. Methyl cyclopropylacetate was prepared in 35% yield from cyclopropanecarbonyl chloride by an Arndt-Eistert reaction in which the decomposition of diazoacetylcyclopropane was carried out by the Newman modification (74), which involves the addition of a solution of silver benzoate in triethylamine to the diazoketone in methanol. Methyl cyclopropylacetate obtained in this way had the same physical properties as a sample prepared by Smith and McKenzie (75) by the methylation of cyclopropaneacetic acid. Smith and McKenzie prepared cyclopropaneacetic acid through condensation of cyclopropanecarbonyl chloride and ethyl diazoacetate, followed by rearrangement of the diazoester, hydrolysis of the resulting malonic ester to cyclopropylmalonic acid and decarboxylation. Attempts to prepare cyclopropaneacetic acid directly

from cyclopropanecarbonyl chloride by an ordinary Arndt-Eistert reaction were reported to be unsuccessful (76).

Preparation of cyclopropylacetonitrile by the reaction of "cyclopropylcarbinyl bromide" and potassium cyanide in aqueous ethanol was described a number of years ago by Von Braun and co-workers (77). No experimental details were given; a product was obtained, b.p. 142-144°, in 60% yields, to which was assigned the structure of cyclopropylacetonitrile. Von Braun and co-workers prepared the bromide by the reaction of N-cyclopropylbenzamide with phosphorous pentabromide (78). More recent work has shown that the product is actually a mixture of cyclopropylcarbinyl, cyclobutyl and allylcarbinyl bromides (38). According to infrared analysis, the mixture has about the same composition as the mixture of bromides obtained by treatment of cyclopropylcarbinol with phosphorous tribromide, which was reported as about 20% cyclobutyl bromide, 65% cyclopropylcarbinyl bromide and 15% allylcarbinyl bromide (38). In the present work, a mixture of bromides was obtained from cyclopropylcarbinol and phosphorous tribromide in yields up to 92%. The product consisted of 5% allylcarbinyl bromide, 20% cyclobutyl bromide and 75% cyclopropylcarbinyl bromide, according to v-p-c analysis, in reasonable agreement with the earlier infrared analysis by Roberts and Masur (38). The best conditions for conversion to nitrile involved treatment of the mixture of bromides with a saturated solution of sodium cyanide in 80% ethanol-water. The mixture of low-boiling

products, b.p. 100-130°, was not investigated thoroughly, but cyclobutyl bromide appears to be one of the many components of this mixture; the other bromides were consumed. The main fraction, b.p. 138-143°, consisted of three components in a ratio of 76: 23: 1 (v-p-c). A fraction rich in the intermediate component was isolated by preparative v-p-c and on the basis of its infrared spectrum was assigned the structure of allylcarbinyl cyanide. The main component was assigned the structure of cyclopropylacetonitrile on the basis of its infrared and n-m-r spectra.* Treatment of the mixture with permanganate solution consumed the open-chain isomer and the cyclic nitrile was reisolated in 95-98% purity. The total yield of nitriles was 50-60%, based on bromide taken and 65-70%, based only on the cyclopropylcarbinyl and allylcarbinyl bromides in the starting material. The overall yield of purified cyclopropylacetonitrile was 48% in a large scale run.

The reduction of cyclopropylacetonitrile with lithium aluminum hydride gave poor results. A small amount of a complex mixture of products containing some aldehyde was obtained, but the bulk of the material went to tar. Similar results were obtained by Renk (56) with allyl cyanide. Apparently, hydrogens at the alpha position in both nitriles are activated and their removal results in anionic polymerization and tar formation.

*The apparent absence of cyclobutyl cyanide in the product suggests that the nitriles are formed by an S_N^2 process.

N,N-Dimethylcyclopropylacetamide was prepared in 54% yield by a modified Arndt-Eistert reaction in which diazoacetylcyclopropane was decomposed in dioxane by the simultaneous addition of silver nitrate solution and dimethylamine. The structure of the amide was assigned on the basis of infrared and n-m-r spectra and elemental analysis. The reduction of the amide with lithium diethoxyaluminumhydride, according to the procedure of Brown and Tsukamoto (70) was run a total of eleven times under varying conditions. The same difficulties discussed earlier in connection with the reduction of amides with alkoxyhydrides (see page 39) were again encountered. Good yields of the 2,4-dinitrophenylhydrazone and the semicarbazone could be obtained by treating the reaction mixture, after hydrolysis, with the desired reagent. The best procedure found for isolation of the aldehyde was to heat the semicarbazone with an equimolar amount of phthalic anhydride and to steam-distill the aldehyde. In this way, an 18% yield of cyclopropylacetaldehyde was obtained. The structure assigned was supported by the infrared spectrum. It was found later that the aldehyde could be obtained in about 95% purity and in 10-25% yield by direct reduction of *N,N*-dimethylcyclopropylacetamide with lithium aluminum hydride at 0°. The difficulties encountered on a preparative scale discouraged further use of this method of synthesis. At this time, the following satisfactory synthesis of cyclopropylacetaldehyde was developed and was used to prepare all the cyclopropylacetaldehyde used later in the decarbonylation studies.

Allylcyclopropane was synthesized in one step in about 50% yield by the reaction of cyclopropylmagnesium chloride and allyl bromide. The product, which was not purified, was identified as allylcyclopropane by comparison with pure allylcyclopropane as prepared by White (79) by an alternate series of reactions (see page 125). Allylcyclopropane from both sources was hydroxylated with performic acid in 85% yield and the resulting diol was cleaved with lead tetraacetate in methylene chloride to give cyclopropylacetaldehyde in yields of 57-68%. The product was shown to be identical with that prepared above by the reduction of N,N-dimethylcyclopropylacetamide and its properties are in general agreement with those reported by Hart and Wyman (40) for cyclopropylacetaldehyde as prepared by catalytic dehydrogenation of 2-cyclopropylethanol. Additional evidence for the structure was obtained from infrared and n-m-r spectra. Difficulty was encountered in preparing a sample of the aldehyde which gave a satisfactory elemental analysis. Similar difficulties were encountered with 1-methylcyclopropanecarboxaldehyde and cyclobutanecarboxaldehyde. Samples of the aldehyde which showed only one peak in their vapor-phase-chromatograms gave consistently low values for carbon and hydrogen. An analytically pure sample was finally prepared by distillation of the aldehyde, after it had been dried over Drierite, in a nitrogen atmosphere; all handling of the distillate was minimized. According to these results, the impure samples of aldehyde probably contained peroxidic compounds, formed on contact with air, which did not appear in the vapor-phase-chromatograms. Satisfactory

analyses were obtained for the 2,4-dinitrophenylhydrazone, p-nitrophenylhydrazone and semicarbazone of cyclopropylacetaldehyde.

Cyclobutanecarboxaldehyde was prepared by two different methods. Cyclobutylcarbinol, obtained by reduction of cyclobutanecarboxylic acid, was oxidized by sodium dichromate in sulfuric acid to cyclobutanecarboxaldehyde in low yield; considerable cyclobutylcarbinol was recovered. A better procedure was found to be the reduction of N-methylcyclobutanecarboxanilide with lithium aluminum hydride, according to Weygand's procedure (80). The yield of cyclobutanecarboxaldehyde was 23%. Cyclobutylcarbinol was also obtained in about 10% yield while about 15% of starting material was recovered in addition to a large amount of undistillable tar. There was also isolated a crystalline solid which was determined to be a polymer of cyclobutanecarboxaldehyde and may be the cyclic trimer, according to its n-m-r spectrum. Evidence for the structure of cyclobutanecarboxaldehyde was obtained from its infrared and n-m-r spectra and elemental analysis (see comments on page 46). The melting point of the 2,4-dinitrophenylhydrazone, for which a satisfactory analysis was also obtained, agreed well with previous literature values (81,69), but there were discrepancies between the physical properties of the aldehyde itself and those reported by Slobodin and Blinova (81) (see Experimental). The yields reported in the above work are by no means optimum since the synthesis was not studied extensively.

Cyclopropylacetonitrile was methylated with sodamide and methyl bromide in liquid ammonia by the procedure of Newman and co-workers (82). A single product, obtained in 65% yield, was determined to be

dimethylcyclopropylacetonitrile by its infrared and n-m-r spectra and elemental analysis. The spectra indicated the complete absence of open-chain isomers; in particular, the n-m-r spectrum showed no vinyl-proton resonances. This result could be contrasted with the exclusive ring opening which accompanies attempted formation of the cyclopropylcarbinyl Grignard reagent (see page 21). The dimethylated nitrile was reduced with lithium aluminum hydride to dimethylcyclopropylacetaldehyde in 80.5% yield. The cyclic structure of the aldehyde was supported by its infrared and n-m-r spectra. Satisfactory analyses were obtained for the aldehyde and its 2,4-dinitrophenylhydrazone.

For comparison with the product obtained on decarbonylation of dimethylcyclopropylacetaldehyde, isopropylcyclopropane was prepared by the following route. Dimethylcyclopropylcarbinol was prepared by the reaction of ethyl cyclopropanecarboxylate and methylmagnesium chloride. The alcohol was dehydrated to isopropenylcyclopropane with concentrated sulfuric acid, according to the procedure of Slabey and Wise (83), and isopropenylcyclopropane was hydrogenated over platinum black to give a mixture of about 75% isopropylcyclopropane and 25% 2-methylpentane. The composition and nature of the product was established by its physical and spectral properties. It was not felt necessary to separate the components for use in the decarbonylation studies.

Decarbonylation Results

Di-t-butyl peroxide was used to initiate the decarbonylation of all the aldehydes in this study at temperatures of 130-140°. In addition, the benzoyl peroxide-initiated decarbonylation of cyclopropylacetaldehyde was also studied. Some of the decarbonylation experiments were run with neat aldehydes, while others were run using 10% solutions of the aldehyde in diphenyl ether as solvent. In the case of aldehydes of boiling point below 120°, the extent of decarbonylation was observed to be less with the neat liquids than with the solutions. Incomplete reaction in the case of the neat liquids is attributed to the lack of contact between the peroxide and the aldehyde, since the latter exists principally in the vapor state at bath temperatures greater than 130°. The extent of reaction was determined on the basis of non-condensable gas collected, which is assumed (for the calculation) to be entirely carbon monoxide. The infrared spectra of the gases from the various decarbonylation experiments indicated that they consisted of mixtures of carbon monoxide, methane and carbon dioxide. In those runs which gave a high yield of gas, carbon monoxide was the principal gaseous product and only very small amounts of methane and carbon dioxide were obtained. In those cases in which low yields of gas were evolved, particularly in the decarbonylation of cyclopropanecarboxaldehyde, much larger proportions of methane to carbon monoxide were obtained. These observations are discussed fully in the Discussion section.

Particular attention was directed to the determination of the nature of the monomeric hydrocarbon product(s) obtained on decarbonylation of the respective aldehydes. In the cases of cyclopropanecarboxaldehyde, 1-methylcyclopropanecarboxaldehyde, cyclobutanecarboxaldehyde and cyclopropylacetaldehyde, the hydrocarbon products were gases which were condensed in cold traps as they distilled out of the reaction flask. The hydrocarbon products from the decarbonylation of 1-phenylcyclopropanecarboxaldehyde and dimethylcyclopropylacetaldehyde were liquids which were separated by fractional distillation from the other components of the reaction mixture. The purity and identity of the monomeric hydrocarbon products were determined through the use of vapor-phase-chromatography (v-p-c) and infrared and nuclear magnetic resonance (n-m-r) spectroscopy. The physical and spectral properties of the products were compared with those of authentic compounds synthesized independently. Except for the products of decarbonylation of isovaleraldehyde and dimethylcyclopropylacetaldehyde in benzyl mercaptan, the decarbonylation products were found to be pure substances, uncontaminated by isomeric hydrocarbons. An estimate of the maximum possible amount of impurity which could be present in the latter cases and pass undetected is about 0.1%. The results are summarized in Table I along with the results found for a typical aliphatic aldehyde, isovaleraldehyde.

Table I

Aldehyde	Extent of Decarbonylation, %	Product
Isovaleraldehyde	91 ^a , 16.5 ^c , 17.4 ^c	Isobutane ^e
Cyclopropanecarboxaldehyde	14.4 ^a , 16.3 ^a	No product isolated
1-Methylcyclopropanecarboxaldehyde	58.7 ^a , 58.9 ^a , 60.0 ^a	Methylcyclopropane
1-Phenylcyclopropanecarboxaldehyde	96.5 ^b	Phenylcyclopropane
Cyclobutanecarboxaldehyde	90.8 ^a , 106 ^a	Cyclobutane
Cyclopropylacetaldehyde	101 ^a , 94.2 ^a , 76.5 ^a , 50 ^b , 31 ^c , 60 ^d	1-Butene
Dimethylcyclopropylacetaldehyde	53.8 ^b , 47.2 ^b , 141 ^a , 55.4 ^f	2-Methyl-2-pentene ^g

^aInitiated by di-*t*-butyl peroxide; solution of aldehyde in diphenyl ether.

^bInitiated by di-*t*-butyl peroxide; neat aldehyde. ^cInitiated by benzoyl peroxide; neat aldehyde. ^dInitiated by benzoyl peroxide; solution of aldehyde in diphenyl ether. ^eContaminated by about 10% of an impurity which is not isobutylene. ^fSolution of aldehyde in benzyl mercaptan.

^gIn the case of the decarbonylation of aldehyde in benzyl mercaptan, product consisted of 82% 2-methyl-2-pentene and 18% isopropylcyclopropane.

No product could be isolated from the decarbonylation of cyclopropanecarboxaldehyde, although the evolved gas did contain a trace of carbon monoxide. Distillation of the residue afforded recovered cyclopropanecarboxaldehyde, cyclopropanecarboxylic acid, acetone, t-butyl alcohol and small amounts of unidentified components, according to v-p-c. 1-Methyl- and 1-phenylcyclopropanecarboxylic acids were isolated in yields of 12-15% and 9.2%, respectively, from decarbonylation of the corresponding aldehydes. In general, the isolation and identification of high-boiling decarbonylation products was difficult because of the small scale of the runs and because of the volatility of diphenyl ether which tended to co-distill with other materials, regardless of the bath temperature used in the distillation.

The decarbonylation of a 1:1 mixture of cyclopropylacetaldehyde and isovaleraldehyde (10% solution in diphenyl ether), initiated by di-t-butyl peroxide, was carried to about 50% completion, according to the volume of gas evolved, and afforded a 1:1 mixture of isobutane and 1-butane. The same result was obtained when an excess of cumene was added to the reaction mixture before the addition of peroxide.

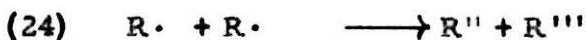
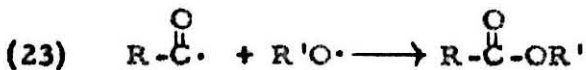
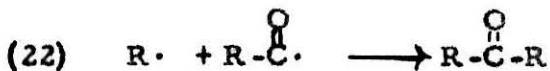
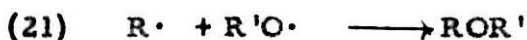
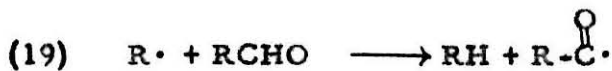
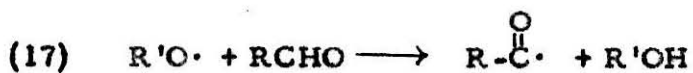
The decarbonylation of dimethylcyclopropylacetaldehyde in an excess of benzyl mercaptan, initiated by di-t-butyl peroxide, gave substantially different results from those obtained with the neat aldehyde or in diphenyl ether. Gas evolution came to 55.4% of theory. The hydrocarbon portion of the product consisted of 82% 2-methyl-2-pentene and

18% isopropylcyclopropane. No isopropylcyclopropane was found in the other runs reported in Table I in which the product was pure 2-methyl-2-pentene.

Discussion of the Decarbonylation Results

A. Cyclopropanecarboxaldehyde, 1-Methylcyclopropanecarboxaldehyde, 1-Phenylcyclopropanecarboxaldehyde.

The general chain-reaction mechanism for the free radical decarbonylation of aldehydes initiated by peroxide is as follows:



Equations 16 and 17 in the above scheme represent initiation steps and 18 and 19 represent chain propagation steps. Possible chain termination processes are given in equations 20-24 and yield dimers, ethers, ketones

and esters, respectively. Equation 24 represents chain termination by disproportionation. While the chain termination products were not investigated in detail in this study, no disproportionation products were observed which indicates that termination by equation 24 is probably not important. Cyclopropanecarboxylic acid and its 1-methyl and 1-phenyl analogs were isolated from decarbonylation of the corresponding aldehydes and may arise from the decomposition on distillation of t-butyl esters derived from coupling of acyl radicals and t-butoxy radicals, according to equation 23.* This process represents a possible chain termination reaction in cases in which the acyl radical does not readily lose carbon monoxide (see further discussion below).

Another reaction which is of importance in chain reactions initiated by di-t-butyl peroxide is fragmentation of t-butoxy radicals into acetone and methyl radicals, according to equation 25.



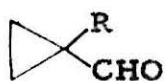
Methyl radicals can, of course, serve as chain initiators and react with aldehyde to give methane and acyl radicals, as in equation 26.



It has been suggested that the extent of fragmentation of t-butoxy radicals

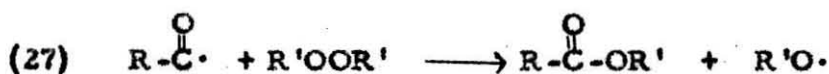
*The source of the carboxylic acids was not checked experimentally. Decomposition of t-butyl esters to give carboxylic acids is known to occur in other systems, usually with acid catalysis (84).

increases as the temperature is raised (85). Thus, the presence of methane and acetone in the products of nearly all the decarbonylation reactions of this study suggests that the reactions of equations 25 and 26 become important at 130-140°.

The results of the decarbonylation reactions of cyclopropanecarboxaldehyde, 1-methyl- and 1-phenylcyclopropanecarboxaldehyde, are summarized on pages 49 and 52. It was found that the reaction of cyclopropanecarboxaldehyde with either di-t-butyl or benzoyl peroxide resulted in only slight gas evolution; the evolved gas consisted principally of methane, and no decarbonylation products were isolated. The extent of gas evolution for the series of aldehydes  increased in the order $R = H < CH_3 < \phi$ and the proportion of carbon monoxide to methane in the evolved gas increased in the same order. Decarbonylation was carried out at comparable temperatures in each case but the length of time required for the extent of gas evolution reported in Table I decreased in the order $R = H > CH_3 > \phi$. The substituted aldehydes gave as their exclusive decarbonylation products methyl- and phenylcyclopropane, respectively. These results agree with earlier studies (see Introduction) in which unsubstituted cyclopropyl radicals were generated only with difficulty, and these and substituted cyclopropyl radicals did not rearrange below 200°.

Consideration of the possible alternate reaction paths of t-butoxy radicals with aldehydes reveals that, in a reaction of moderate chain length, nearly all the t-butoxy radicals generated will react with

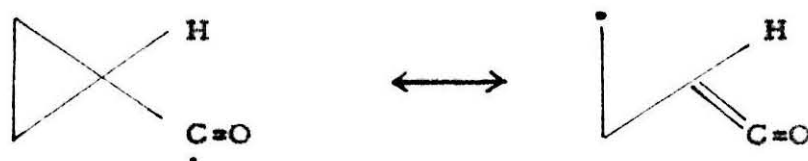
aldehyde (eq. 17) to give acyl radicals which will then enter the chain sequence (eqs. 18 and 19), and relatively few t-butoxy radicals will react according to equations 25 and 26.* In such a process, the evolved non-condensable gas will be almost entirely carbon monoxide, and this is the case for most decarbonylation reactions initiated by di-t-butyl peroxide at 130-140°. In some cases, however, the abstraction step may proceed as usual but, for reasons to be discussed below, the chain length of the process may be very short, chiefly because of a slow decarbonylation step (eq. 18). In such a situation, fragmentation of t-butoxy radicals will become more important relative to decarbonylation and methane will be evolved in preference to carbon monoxide. Thus, the experimental observation that more methane was evolved relative to carbon monoxide in the decarbonylation of cyclopropanecarboxaldehyde than in the cases of its 1-methyl and 1-phenyl analogs may be due to the reluctance of unsubstituted cyclopropanecarbonyl radicals to lose carbon monoxide (eq. 18) in competition with a steady rate of production of methane (eqs. 25 and 26). The fate of those acyl radicals which do not undergo decarbonylation is apparently to couple with t-butoxy radicals (eq. 23) and/or to react with peroxide to form t-butyl esters, thus regenerating t-butoxy radicals, according to equation 27.



*Walling (85) suggests that the activation energy for t-butoxy radical decomposition is higher than that for hydrogen abstraction.

There is evidence that the activation energy for loss of carbon monoxide from an acyl radical is significant. For instance, acyl radicals can be trapped to give acyl chlorides when decarbonylation is attempted in carbon tetrachloride solution (4, 86). Calvert and Gruver (87) found that the enthalpy change on decomposition of the acetyl radical into carbon monoxide and methyl radicals is + 9.7 kcal./mole. For the other aliphatic aldehydes, the enthalpy of decarbonylation, reaction 18, would be expected to be less than 9.7 kcal./mole because of inductive and hyperconjugation effects. The observation that cyclopropanecarbonyl radicals and benzoyl radicals (derived from benzaldehyde) (88) react exclusively by paths other than decarbonylation* implies that the activation energy for homolytic breakage of the C-C bond between the carbonyl group and the ring is large in these systems, probably greater than 9.7 kcal./mole. This result is reasonable on the basis of the following considerations. First, benzoyl and cyclopropanecarbonyl radicals may be stabilized by considerable resonance relative to phenyl and cyclopropyl radicals, respectively; the resonance in the cyclopropanecarbonyl radical, if important, might involve carbon-carbon hyperconjugation, as illustrated below.

*Cyclopropanecarbonyl radicals react apparently by either equations 23 and/or 27. Benzoyl radicals add to benzaldehyde to give radicals which subsequently dimerize (88).



Second, the bond strength of the R-CO bond may be large for R=cyclopropyl or phenyl in comparison with R=alkyl because of hybridization effects. For both R=phenyl and cyclopropyl, the orbital used in bonding with the carbonyl group should have considerably more s-character than for R=alkyl and the bond should therefore be relatively stronger in the phenyl and cyclopropyl cases. It can be seen from the bond dissociation energies given in Table II, taken from Walling's extensive compilation (89), that, for X = H, CH₃ and Cl (and for other groups not included in

Table II

Bond Dissociation Energies, kcal./mole

R-X	R-H	R-CH ₃	R-Cl
Methyl-	102	84.2	88.6
Ethyl-	98		
Isopropyl-	94		
<u>t</u> -Butyl-	90		
Vinyl-	(104-122) ^a	109	104
Phenyl-	102	88.6	85.6
Propargyl-	121		

^aIn doubt.

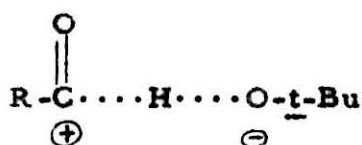
Table II), the energies of phenyl-X, vinyl-X and propargyl-X bonds are large in comparison with those of methyl-X and alkyl-X bonds. That is,

bonds formed with sp^2 - and sp -orbitals are stronger than bonds formed with sp^3 -orbitals. According to theories of Coulson and Moffitt (90) and Walsh* (91), the exocyclic C-H bonds in cyclopropane are formed with orbitals with close to sp^2 hybridization. Thus, cyclopropyl C-X bonds are predicted to be strong compared with other aliphatic or alicyclic C-X bonds. Thus, the results obtained in this study are in keeping with this theory as is the observation that it is more difficult to break a cyclopropyl C-H bond homolytically than it is in corresponding aliphatic cases (see Introduction, pages 24 AND 25).

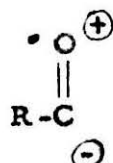
The observation that considerable cyclopropanecarboxaldehyde was recovered from the reaction with di-t-butyl peroxide (a much smaller amount of the 1-methyl analog was recovered in the corresponding case) indicates that other factors may be important in addition to those discussed above. In particular, hydrogen abstraction from cyclopropanecarboxaldehyde by t-butoxy radicals may be relatively difficult in comparison with abstraction from aliphatic aldehydes. There have been only few measurements of aldehyde C-H bond dissociation energies

*According to Coulson and Moffitt (90), cyclopropane is best described in orbital terms as follows. The bonding orbitals which hold the ring together have their symmetry axes at an angle of 22° with respect to the bond direction. These "best" orbitals (i. e., those that minimize the energy of the cyclopropane molecule) turn out to be $sp^{4.12}$ -orbitals (92), which simply means that they have 1 part s-character for 4.12 parts p-character. The exocyclic bonds, according to this model, are formed with $sp^{2.28}$ -orbitals and an exocyclic angle of 116° is predicted, in comparison with an experimental value of 118° . An alternate description of cyclopropane has been given by Walsh (91). In this model, part of the bonding in the plane of the ring is due to overlap of p-orbitals. The remaining three sp^2 -orbitals on each carbon are set up with the

for RCHO as R is varied (87). Burrell and Trotman-Dickenson (93) have recently determined that the rate of abstraction of aldehyde hydrogens by methyl radicals in a series of aliphatic aldehydes was the same for all the aldehydes studied, although there was a large variation in activation energies. However, in the present case, polar structures such as XLV may contribute appreciably to the transition state for abstraction by peroxy radicals (85).



XLV



XLVI

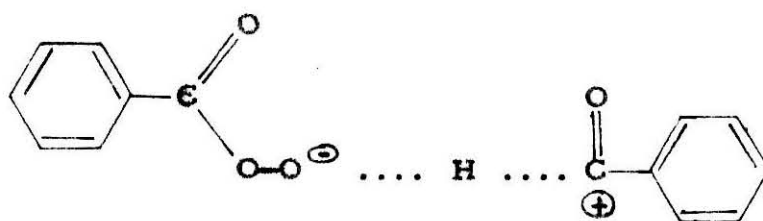
To the extent that XLV is important, R groups in RCHO would be expected to destabilize the transition state in increasing order of their electron-withdrawing inductive effects. On the other hand, carbonyl radicals are said to be stabilized by resonance in which structures such as XLVI are important, according to Walling (94). **R groups should

plane of their axes perpendicular to the plane of the ring in such a way that one orbital points toward the center of the ring while the other two orbitals are used in bonding to exocyclic substituents. Part of the bonding holding the ring together is thus provided by the overlap of three sp^2 -orbitals in the center of the ring. Most important for our purposes, both models predict that the exocyclic cyclopropyl orbitals have very close to sp^2 hybridization.

**It should be noted that in order for such resonance to take place, a distorted carbonyl radical structure must be envisioned, since such resonance implies interaction between sp^2 -orbitals on carbon and p-orbitals which are used in forming the carbonyl π -bond and which are normally perpendicular to the plane of the three sp^2 -orbitals. An alternate rationalization is that an electron is being promoted from an unshared pair on oxygen into an antibonding orbital.

stabilize such structures in increasing order of their electron-withdrawing inductive effects. The two effects therefore oppose each other and, depending on their relative importance, the ease of abstraction of hydrogen atoms from aldehydes by peroxy radicals may be insensitive to variation in the R group or may vary in a predictable manner with the inductive effect of R.

Walling and McElhill (95) found a definite but not large substituent effect ($\rho = -0.8$) in the reaction of substituted benzaldehydes with *p*-chloroperbenzoate radicals in acetic anhydride solution. The ease of breaking of the aldehyde C-H bond was observed to vary with the substituent on the aromatic ring in accord with polar contributions such as XLVII to the transition state for the reaction. Extrapolation of this



XLVII

result to the present case of the reaction of aldehydes with *t*-butoxy radicals may not be justified because of the change in the nature of the acceptor radical (*t*-butoxy vs. perbenzoate) and the change in the solvent (diphenyl ether or aldehyde vs. acetic anhydride). However, if the extrapolation is made, then it follows that cyclopropanecarboxaldehyde and benzaldehyde may be relatively unreactive (compared with typical aliphatic aldehydes) toward *t*-butoxy radicals because of the electron-

withdrawing inductive effects of phenyl and cyclopropyl (96) groups.

Clearly, more experimental work is needed to clear up these problems.

The decrease in the activation energy of the decarbonylation step (eq. 18) for 1-methyl and 1-phenylcyclopropylcarbonyl radicals relative to the cyclopropylcarbonyl radical (as evidenced by the rate and extent of carbon monoxide formation and the isolation of only small quantities of the corresponding carboxylic acids) may be due chiefly to the enhanced stability of 1-methylcyclopropyl and 1-phenylcyclopropyl radicals in comparison with cyclopropyl radicals. In order for substituents such as methyl and phenyl to exercise maximum stabilization of an adjacent radical center by resonance interaction, the substituent should be coplanar with the radical center. In the present case, the attainment of coplanarity is expected to increase the strain energy (I-strain) in the system because of concomitant hybridization changes in the cyclopropane bonding orbitals. This qualitative conclusion follows from the Coulson-Moffitt (90) and Walsh(91) descriptions of cyclopropane, but it is difficult to estimate the magnitude of the effect. Although the non-planar cyclopropyl radical may possibly be theoretically more stable than the planar radical, the barrier to inversion or to the attainment of planarity is probably small, as has been shown by Applequist and Peterson (44).

The observation that ring opening of cyclopropyl radicals does not occur below 200° (see page 24) is, at first, surprising since ring opening would appear to be energetically favored by at least 30

kcal./mole, as estimated by the relief of steric strain on isomerization and the formation of an allyl radical with a resonance energy of approximately 25 kcal./mole (89). The energy barrier to isomerization thus appears to be large but is surmountable above 200°. Significantly, such a large barrier does not appear to exist for the cyclopropyl cation which isomerizes to the allyl cation at low temperatures (43b). Since, to a first approximation, the resonance energies of allyl cations, radicals and anions are the same, the above observations can be rationalized by postulating that cyclopropyl cations have a higher free energy than cyclopropyl radicals, whereas the transition states for the isomerization of both species are more comparable in energy. Therefore, the activation energy for isomerization of the cation would be less than for the radical, even though a similar mechanism might be operative in both cases.

B. Cyclobutanecarboxaldehyde, Cyclopropylacetaldehyde and Dimethylcyclopropylacetaldehyde.

The results of the decarbonylation of cyclobutanecarboxaldehyde, cyclopropylacetaldehyde and dimethylcyclopropylacetaldehyde are given in Table I, page 51. Whereas similar product distributions are obtained from carbonium ion reactions of cyclobutyl and cyclopropylcarbinyl derivatives (see page 18), cyclobutanecarboxaldehyde underwent free radical decarbonylation to give exclusively cyclobutane while 1-butene was the sole product of decarbonylation of cyclopropylacetaldehyde. The observed lack of rearrangement of the cyclobutyl radical is

in agreement with earlier studies in which cyclobutyl radicals, generated by alternate methods, also reacted without rearrangement (see page 25). The exclusive ring-opening which was found to occur on decarbonylation of cyclopropylacetaldehyde at 80° and 130-140° is in contrast with the results of the photochlorination of methylcyclopropane which afforded mixtures of cyclopropylcarbiny and allylcarbiny chlorides (see page 27); no cyclobutyl derivatives were obtained in either of these studies. Dimethylcyclopropylacetaldehyde was found to react exclusively with ring opening in the normal decarbonylation reactions while a mixture of cyclic and ring-opened products was obtained when the reaction was carried out in the presence of benzyl mercaptan. This result is therefore similar to that found when unsubstituted cyclopropylcarbiny radicals were generated in the presence of chlorine.

The independent courses of reaction followed by cyclobutyl and cyclopropylcarbiny derivatives in free radical reactions, in contrast to their behavior in corresponding carbonium ion reactions, indicate that the common "non-classical" bicyclobutonium-type intermediates which have been postulated for interconversion in carbonium ion reactions (1) are not involved in free radical reactions. This diverse behavior is in accord with the predictions of simple molecular orbital (L.C.A.O.) calculations. An orbital diagram of an unsymmetrical bicyclobutonium intermediate and its projection, as postulated (1) for the carbonium ion reaction, are shown in Figure 2. The resonance integrals assumed for four rather extreme examples of such a structure are given in Table III

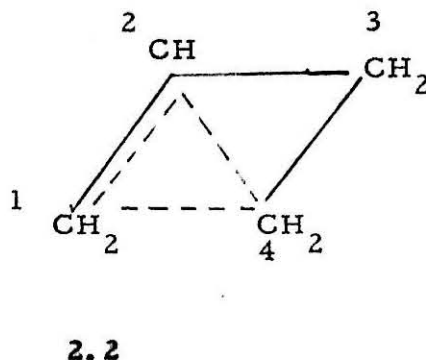
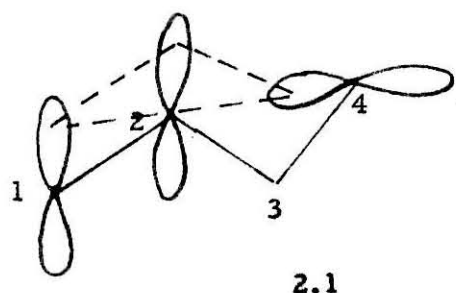


Figure 2

along with the calculated electronic energy levels. All Coulomb integrals were taken as α . It should be noted that the energy levels calculated for the three orbitals of Structure A are the same for any three-fold symmetrical system of three orbitals in which the same values of the resonance and Coulomb integrals are assumed, such as the tri-cyclobutonium cation XXXV (Page 20), the cyclopropenium cation and Dewar's simple formulation of bridged ethylene intermediates (97).

Table III

	Bicyclobutonium Structures			
	A	B	C	D
1-2 Resonance Integral, β	1	0.8	1	1
1-4 Resonance Integral, β	1	0.4	0.5	0.2
2-4 Resonance Integral, β	1	1	0.5	1

Calculated Electronic-Energy Levels :

$\alpha+2\beta$	$\alpha+1.5\beta$	$\alpha+1.4\beta$	$\alpha+1.6\beta$
$\alpha-\beta$	$\alpha-0.4\beta$	$\alpha-0.4\beta$	$\alpha-0.2\beta$
$\alpha-\beta$	$\alpha-1.1\beta$	$\alpha-1.0\beta$	$\alpha-1.4\beta$

The delocalization energies calculated for carbonium ions, free radicals and carbanions in bicyclobutonium configurations (A-D) were obtained as usual by filling the orbitals with two, three and four electrons, respectively, and correcting for the electronic energy of a simple olefin (2α or 2β). The results are given in Table IV in units of β . Usually β is considered to be about -20 kcal./mole (98).

Table IV

Delocalization Energies of Bicyclobutonium Structures, Units of β

	A	B	C	D
Carbonium Ion	2.0	1.0	0.8	1.2
Free Radical	1.0	0.6	0.4	1.0
Carbanion	0.0	0.2	0.0	0.8

The validity of the above calculations is uncertain. First, it should be noted that if proper account were taken of interelectronic repulsions, the delocalization energies of the radicals and anions would certainly be substantially lowered relative to the carbonium ions. Second, the calculated delocalization energies must be corrected for angle strain and non-bonded repulsions if accurate intercomparisons are to be made between the various structures A-D. Nonetheless, several important qualitative conclusions might be drawn from the results. The first two electrons used to fill the molecular orbitals, giving rise to bicyclobutonium cations, go into strongly bonding orbitals.

These configurations are thus predicted to have substantial electron delocalization energies relative to non-delocalized allylcarbinyl cations. The cation with the largest predicted delocalization energy (A) is, significantly, the one in which the most symmetrical orbital overlap was assumed; the delocalization decreases as the 1-4 interaction decreases, that is, as the structure becomes increasingly homoallylic. Addition of one or two more electrons to each system, such as would give rise to the corresponding bicyclobutonium free radicals and anions, respectively, requires the use of more or less antibonding orbitals. Therefore, the electron delocalization energies of the radicals and anions are predicted to be less than those of the corresponding cations. The carbanions, as can be seen from Table IV, are predicted to have little net stabilization except in the quite unsymmetrical Structure D which is almost a "pure" homoallylic configuration. Bicyclobutonium radicals are predicted to have the greatest delocalization energy with Structure A, in which equal overlap is assumed, and in Structure D, with only a weak 1-4 interaction. These calculations confirm the prediction that bicyclobutonium intermediates should be more important relative to classical intermediates in the case of the carbonium ions than in the cases of the corresponding radicals and anions.

The ring opening observed in the decarbonylation of cyclopropylacetaldehyde and dimethylcyclopropylacetaldehyde will now be considered in more detail. First, let us assume that the individual substituted and

unsubstituted cyclopropylcarbinyl and allylcarbinyl radicals can have separate existences. Then, we might assume that the enthalpy change associated with the rearrangement of cyclopropylcarbinyl radicals to allylcarbinyl radicals is due only to relief of strain. Of course, the correctness of this assumption would depend on the relative degree that a cyclopropyl group, as R, could stabilize a radical center $\text{RCH}_2\cdot$ as compared to an allyl group, as R. The magnitude of the relief of strain in interconversion of the hypothetical unstabilized radicals might be taken as the enthalpy of isomerization of cyclopropane to propylene (-7.9 kcal./mole) (99) although the enthalpy of isomerization of methylcyclopropane to 1-butene (unknown) would clearly be a better choice knowing that alkyl groups stabilize small rings.

There are additional factors involved in the rearrangement of a tertiary dimethylcyclopropylcarbinyl to a primary 6,6-dimethylallylcarbinyl radical. If we again neglect stabilization by the three-membered ring, the cyclic radical should be stabilized by about 8 kcal./mole* through hyperconjugation involving the two α -methyl groups while the two methyl groups on the double bond would be expected to stabilize the primary open-chain radical to the extent of about 5 kcal. mole.**

*Successive substitution of methyl groups for hydrogen in methane decreases the C-H bond dissociation energy by 4 kcal./mole per methyl group (see Table I). This is taken to imply stabilization of the resulting radical, presumably by hyperconjugation.

**The heats of hydrogenation of olefins are decreased by substitution of methyl groups on the double bond by an average value of about 2.5 kcal./mole per methyl group (100).

The net enthalpy change in the hypothetical isomerization is therefore estimated to be about -5 kcal./mole. Thus, provided the three-membered ring does not provide any significant stabilization of an adjacent radical center, then for both the cyclopropylcarbinyl and dimethylcyclopropylcarbinyl cases, ring opening to allylcarbinyl-type radicals is calculated to be exothermic by 5-8 kcal./mole.

Although the energy change on isomerization of a cyclopropyl to an allyl radical is calculated to be about -30 kcal./mole, as estimated from the relief of steric strain and the resonance stabilization of the resulting allyl radical, there seems to be a substantial barrier to this isomerization, which does not take place below 200° (see pages 24, 62-63). The enthalpy changes calculated for ring opening of cyclopropylcarbinyl and dimethylcyclopropylcarbinyl radicals are much smaller (about -8 and -5 kcal./mole, respectively) yet ring opening was found to occur readily in the decarbonylation reactions at moderate temperatures. If we adhere to the assumption that the decarbonylation reactions of the cyclic aldehydes produce radicals which are not significantly stabilized by the three-membered rings, then this difference in behavior might be ascribed to the possibility of formation of a low-energy intermediate (or transition state) for the latter cases.

Examination of an orbital representation of a cyclopropylcarbinyl radical, Figure 3.1, shows that good overlap is possible between a p-orbital at the carbinyl position (C_1) and one of the $sp^{4.12}$ -orbitals used

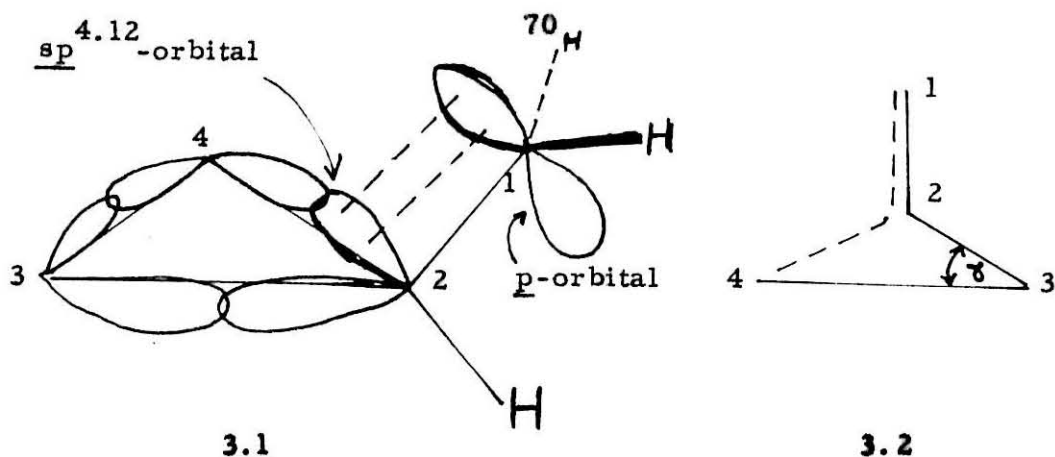


Figure 3

by the neighboring carbon atom (C_2) in bonding to the other ring carbons. If such 1-2 overlap were important, it would weaken the bonding between C_2 and C_4 giving a radical which might be represented as in the projection diagram, Figure 3.2. This radical can be called a "non-classical" homoallylic radical and is different from the bicyclobutonium structures considered previously (Fig. 2) because of the neglect of 1-4 interaction.

Calculation of the delocalization energies of homoallylic carbonium ions has been carried out by Simonetta and Winstein (98). In their calculations, the 2-4 distance was varied and a correction was made for the strain introduced as the angle was compressed at C_3 . The simple L.C.A.O. theory suggests that the molecular orbitals for such a system correspond to those of allylic systems. The electrons needed to form the radical and anion thus go into non-bonding and not antibonding orbitals. Therefore, the delocalization energies of homoallylic carbonium ions, free radicals and carbanions should be identical to the approximation that interelectronic repulsions may be neglected. The delocalization energies calculated by Simonetta and Winstein (98) for the cations

have on this basis been used for the radicals and anions. These values are given in Table V. When the corrections for angle strain, relative

Table V

$R_{2-4}, \text{\AA}$	Resonance Integral, Units of β	Resonance Energy, kcal/mole	Strain Energy, kcal/mole		Total Energy, kcal/mole	
			B=59	B=66	B=59	B=66
2.51	0.30	1.8	0.0	0.0	1.8	1.8
2.35	0.47	4.2	0.9	1.1	3.3	3.1
2.15	0.68	8.3	2.8	3.2	5.5	5.1
1.95	0.88	13.2	6.1	7.0	7.1	<u>6.2</u>
1.75	1.03	17.4	10.2	11.6	<u>7.2</u>	5.8
1.63	1.08	18.8	12.9	14.7	5.9	4.1
1.54	1.11	19.7	14.7	16.8	5.0	2.9

B = energy of a carbon-carbon bond.

to an open-chain model, * are included, it is seen that the calculated net delocalization energy (- "total energy," Table V) of the homoallylic system goes through a maximum at particular values of the 2-4 distance, corresponding to the underlined energy values. The 2-4 distance corresponding to maximum stability comes out to be 1.75-1.95 \AA and

*The calculation of the angle strain was made assuming that hybridization at C_1, C_2 and C_4 was always sp^2 and that at C_3 was always sp^3 . Winstein and Simonetta suggest that rehybridization on forming the homoallylic structure should increase the calculated resonance energy and decrease the calculated strain energy. Indeed, the estimates of the strain energy given in Table V appear high since the strain energy in cyclopropanes, corresponding to the shortest 2-4 distance used in the calculation, appears to be about 8 kcal./mole relative to open-chain compounds, rather than 15-17 kcal./mole, as calculated here.

corresponds to a structure in which angle γ , Figure 3.2, is 72° (assuming the 2-3 and 2-4 distances are 1.54 \AA) and the 1-4 distance is $3.0\text{-}3.2 \text{ \AA}$. For comparison, the 2-4 distances for hypothetical cyclopropylcarbiny and allylcarbiny structures were calculated on the basis of reasonable geometries to be 1.54 \AA and 2.51 \AA , respectively. On this basis, the calculated most stable homoallylic structure is intermediate between a cyclopropylcarbiny and an allylcarbiny structure and more closely resembles the cyclic system. Based on the calculated coefficients of the atomic orbitals in the bonding molecular orbital, the most stable configuration was calculated by Simonetta and Winstein (98) to be equivalent to resonance between allylcarbiny and cyclopropylcarbiny structures with the following contributions from each form:

Allylcarbiny	Cyclopropylcarbiny	
48.5	51.5	B = 59
56	44	B = 66.6

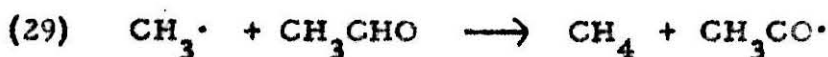
The 1-4 distance in this most stable structure is sufficiently large that the neglect of 1-4 interaction, assumed above, is justified. Since electron repulsion effects, as discussed earlier, would be expected to decrease the delocalization energy of free radicals and carbanions relative to the corresponding carbonium ions, the delocalization energies of Table V are maximum values for these quantities as applied to radicals and anions.

Several significant qualitative conclusions can be drawn from the results of the calculations. First, at least some degree of homoallylic resonance stabilization is to be expected for substituted and unsubstituted cyclopropylcarbinyl radicals and anions (if such exist as separate entities). Second, this kind of stabilization should be less important for the corresponding allylcarbinyl radicals (cf. Table V) which means that the values for the enthalpies of isomerization calculated earlier (5-8 kcal./mole) are probably considerably too large. Third, the theory suggests that homoallylic "non-classical" radical and anion intermediates may well be as important relative to the corresponding classical intermediates and non-delocalized starting materials as the corresponding carbonium ion intermediates. Certainly, on the basis of the available evidence, one must not exclude them from consideration as intermediates in the free radical and carbanion reactions of cyclopropylcarbinyl derivatives. In fact, as mentioned earlier, postulation of such intermediates provides clarification for the facile ring openings observed in the decarbonylation reactions.

Based on the experimental results and the considerations given above, the following alternative mechanistic schemes are reasonable for the rearrangements observed in the decarbonylation of cyclopropylacetaldehyde and dimethylcyclopropylacetaldehyde. For economy, these will be presented only for the unsubstituted case, but apply to substituted cases as well. (1) Cyclopropylcarbinyl radicals are formed by decarbonylation of $\text{RCO}\cdot$ and then rearrange either partially or completely,

depending on their lifetimes, to more stable allylcarbinyl radicals via a homoallylic transition state or an unstable homoallylic intermediate, such as is represented in Figure 3. (2) "Non-classical" homoallylic radical intermediates are produced directly when $\text{RCO}\cdot$ loses carbon monoxide and react to give allylcarbinyl or mixtures of allylcarbinyl and cyclopropylcarbinyl products according to the reaction conditions.*

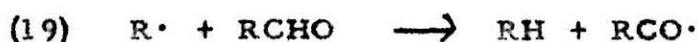
The present experimental data are inadequate to permit a decision to be made between these mechanistic alternatives. The observation that the chlorination of methylcyclopropane gave mixtures of cyclic and ring-opened products whereas decarbonylation of cyclopropylacetaldehyde proceeded exclusively with ring opening can be rationalized as follows. The enthalpies of reaction of a methyl radical with chlorine and with acetaldehyde, equations 28 and 29, respectively are calculated



on the basis of bond dissociation energies (101) to be -22 and -13 kcal./mole, respectively. The latter value is obtained if one assumes a value of 89 kcal./mole for the strength of the aldehyde C-H bond of acetaldehyde, as found by Calvert and Gruver (87). For the corresponding

*The possibility that cyclopropylcarbinyl radicals are formed first and then immediately isomerize to more stable "non-classical" homoallylic radicals is essentially experimentally indistinguishable from mechanism (2) and will not be considered explicitly in further discussion.

reactions of a radical $R\cdot$ in place of $CH_3\cdot$, equations 30 and 19 , where $R\cdot$ is expected to have considerable resonance stabilization, the

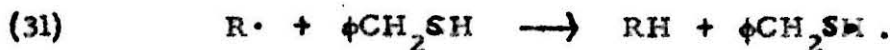


values of ΔH will both be less negative by the amount of such stabilization.* In any case, however, the reaction of $R\cdot$ with chlorine is predicted to be very much faster than reaction with aldehyde. Thus, the experimental results can be rationalized in terms of mechanism (1) by considering that chlorine is able to trap some of the cyclic radicals before they isomerize to allylcarbinyl radicals. (It should be remembered that chlorine cannot prevent all rearrangement of the neophyl radical (6), a process believed to have an activation energy of 7-8 kcal./mole (5).) The aldehyde, on the other hand, should react relatively slowly with alkyl radicals, thus resulting in an increased lifetime for the cyclic radicals and an increased probability for their rearrangement. The data are also compatible with mechanism (2) since a highly effective radical trap such as chlorine should not be very selective in choosing between two possible sites of reaction on a "non-classical" radical, thus resulting in a mixture of products. The observation that only the product corresponding to the allylcarbinyl radical is formed in the decarbonylation

*For the purposes of this argument, a constant aldehyde C-H bond dissociation energy is assumed for all aldehydes. For a detailed discussion of this question, see page 59 ff.

reactions in the absence of mercaptan requires, according to mechanism (2), that aldehyde molecules, which are less reactive and hence more selective than chlorine molecules toward radicals, show considerable selectivity in choosing only one of the two possible sites of reaction on the "non-classical" radical intermediate. Such extreme selectivity would indeed be expected if this step in the chain were at all slow since the reaction of a homoallylic radical with aldehyde would be some 5-8 kcal./mole more favorable if the open-chain rather than the cyclic hydrocarbon were formed. If this energy difference were to be reflected in the energies of activation (and indeed most of it might be if $R\cdot$ were sufficiently stable that reaction 19 were endothermic), the ratio of rates at the two positions of the "non-classical" radical at 100° would be on the order of 10^2 - 10^4 .

The isolation of cyclic hydrocarbon product when the decarbonylation of dimethylcyclopropylacetaldehyde was carried out in the presence of benzyl mercaptan is significant. Mercaptans are known to be efficient chain transfer agents (102). In the present case, reaction of a radical $R\cdot$ with benzyl mercaptan, equation 31, is expected to be favored over

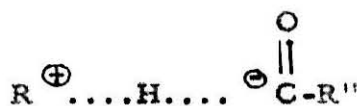


reaction with aldehyde, equation 19. The bond dissociation energy for the S-H bond of benzyl mercaptan has not been determined, but the values for methyl and ethyl mercaptan are 88.8 and 86.8 kcal./mole, respectively (103). If a value of about 87 kcal./mole is assumed for the present

case, reaction 31 is then expected to be some 2 kcal./mole more exothermic than reaction of R^\cdot with the aldehyde. Moreover, the activation energy for attack on the mercaptan might be decreased by polar contributions such as XLVIII to the transition state for the reaction and such contributions (XLIX) might not be expected to be as important in the corresponding reaction with aldehyde. Therefore, the radical chain

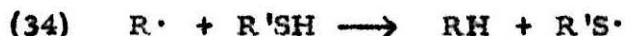


XLVIII



XLIX'

should be modified in the presence of mercaptan* as represented below.



One effect would be that the lifetime of R^\cdot should be shortened in the presence of benzyl mercaptan. Such behavior has been postulated previously to account for reduction in the extent of rearrangement of the neophyl radical when the radical was generated by the decarbonylation of neophylcarboxaldehyde in the presence of benzyl mercaptan (11),

*Striking catalysis of decarbonylation by mercaptans has been noted previously and was interpreted in terms of equations 32-34 (104).

and also for the increase in nortricycyl product at low mercaptan concentrations in the addition of *p*-thiocresol to norbornadiene (28). Formally, a similar result was obtained in this study in that the extent of ring opening resulting from decarbonylation of dimethylcyclopropylacetaldehyde was reduced in the presence of benzyl mercaptan. The result can be rationalized according to mechanism (1) or (2), page 73, by the same arguments used earlier to rationalize the chlorination results. That is, the mercaptan, due to its excellent scavenging properties, is either able to trap some of the dimethylcyclopropylcarbinyl radicals before they isomerize (mechanism (1)), or alternatively, as a reagent of high reactivity and low selectivity, it shows little discrimination between reaction at the two possible sites of a "non-classical" radical (mechanism (2)).

Competitive decarbonylation of cyclopropylacetaldehyde and isovaleraldehyde did not help in settling these questions. A 1:1 mixture of aldehydes afforded, after about 50% reaction, an approximately 1:1 mixture of products, although in both runs the products of decarbonylation of isovaleraldehyde were in excess.* One could interpret this result by saying that the rate constants for initiation, termination and, most important, propagation are about the same for both aldehydes, or else

*The amount of 1-butene in the hydrocarbon portion of the product in two runs was 36% and 42% (see Experimental for details). Since the reproducibility of the result was not determined, differences between the actual product composition and a 1:1 product composition may or may not be significant.

that if anchimeric assistance is important in the formation of any of the intermediates involved, it is largely cancelled out by some (perhaps fortuitous) combination of rate constants.

A decision among mechanisms (1) and (2) might be obtained from a study of the effect of changing the concentration of benzyl mercaptan on the relative amounts of cyclic and open-chain products produced on decarbonylation of dimethylcyclopropylacetaldehyde. Provided that chain transfer with mercaptan is highly efficient, the proportion of cyclic product should increase with increasing concentration of mercaptan, according to mechanism (1), while the proportions of products should be relatively constant, according to mechanism (2). It would also be particularly desirable to study the decarbonylation of cyclopropylacetaldehyde in the presence of benzyl mercaptan to see if cyclic products can be isolated in this case also. Furthermore, if "non-classical" intermediates are involved in the decarbonylation of cyclopropylacetaldehydes, such intermediates might also be generated on decarbonylation of the corresponding allylacetaldehydes. In particular, this mechanism suggests that one might be able to isolate cyclic products on decarbonylation of (γ,γ -dimethylallyl)-acetaldehyde in the presence of benzyl mercaptan. It would be difficult to account for the formation of cyclic products in this reaction by a mechanism involving only classical radical intermediates. However, failure to isolate cyclic products from such a reaction would not necessarily rule out the "non-classical"

radical because the radical conformation may be quite unfavorable at the instant of decarbonylation for formation of a homoallylic radical. Ring closure might not be able to compete with chain transfer.

In all previous cases in which alternative mechanisms were considered to explain the course of a free radical rearrangement (see Introduction), a mechanism involving classical intermediates was always preferred by the authors to one involving "non-classical" intermediates, on the basis of their experimental data. The argument against "non-classical" radical intermediates was usually negative, that is, there was no evidence compelling the postulation of "non-classical" intermediates. If one uses Occam's Razor (105) to decide that "non-classical" intermediates should only be invoked when classical intermediates do not suffice to explain the experimental results, then mechanism (1), involving purely classical radical intermediates and where the homoallylic structure, Figure 3, might figure importantly only as a transition state for the isomerization, appears to be favored. However, the cogency of the theoretical arguments for "non-classical" radicals on pages 69 ff. considerably diminishes the validity of Occam's dictum and any definite decision on the point at issue must, of course, await further experimental results.

General Comments

A striking feature of the results of studies of cyclopropylcarbinyl and cyclobutyl derivatives in free radical reactions is the total lack of interconversion of these structures as compared with the extensive interconversion observed in carbonium ion reactions. Renk's studies (56) of isotopically labeled derivatives showed that there was essentially no carbon shuffling associated with the free radical reaction while extensive shuffling accompanies the carbonium ion reactions (see page 18 ff.). In addition, dimethylcyclopropylcarbinyl derivatives react predominantly with ring opening in free radical reactions while similarly constituted derivatives react with little or no ring opening in kinetically-controlled carbonium ion reactions; furthermore, isomeric open-chain derivatives afford cyclic products in such carbonium ion reactions. Taken together, these contrasting observations provide support for the interpretation of the carbonium ion reactions in terms of the "non-classical" intermediates(1).

The absence of free radical rearrangements of many types common with carbonium ions has already been alluded to in the Introduction. There are no authenticated examples of 1,2-migrations of saturated alkyl groups or hydrogen atoms in free radical reactions, although it can hardly be maintained that the really favorable cases for such migrations have all been studied. However, the bridged radical structures which would be involved as intermediates or transition states

in such migrations can be predicted (see page 64ff) to have much less delocalization energy than the corresponding highly-stabilized bridged carbonium ions;

The observed free radical rearrangements fall into one of two categories. There are those, including all the low-temperature rearrangements, for which transition states can be formulated which are basically allylic or homoallylic in character. The general favorableness of such rearrangements is in agreement with predictions of simple molecular orbital theory since allylic and homoallylic radicals, as contrasted to other types of mesomeric radicals, do not require the use of antibonding orbitals. The other class of rearrangements, as exemplified by the studies of Rust and Collamer (page 9) and Berson and co-workers (page 12) appear to occur as a result of fragmentation and recombination at high temperatures. The high temperature isomerization of cyclopropyl and cyclobutyl radicals might be regarded as related examples of internal fragmentations.

III. EXPERIMENTAL

All melting points and boiling points are uncorrected. Elemental analyses were performed by Dr. Adalbert Elek, Elek Microanalytical Laboratories, Los Angeles, California and by Midwest Microlab, Inc., Indianapolis, Indiana. Most of the infrared absorption spectra were determined using a Perkin-Elmer double-beam recording infrared spectrophotometer, Model 21. Some spectra were determined with a Beckman infrared spectrophotometer, Model IR -7. Vapor chromatograms were obtained with a Perkin-Elmer Vapor Fractometer, Model 154-C. The nuclear magnetic resonance spectra were obtained at 60 Mc. with the Varian Associates high resolution spectrophotometer (V-4300B) with 12-inch magnet and equipped with a flux stabilizer.

Cyclopropanecarboxaldehyde was prepared by the method of Smith and Rogier (68). A solution of 7.1 g. (0.187 mole) of lithium aluminum hydride in 350 ml. of dry ether was added over a period of 30 min. to a solution of 45.6 g. (0.68 mole) of cyclopropyl cyanide (107) in 220 ml. of dry ether, cooled in a Dry Ice-acetone bath to -80° . The mixture was stirred in the cooling bath for 15 min. The bath was removed and the temperature of the mixture was allowed to rise to room temperature over a period of 2 hr. No vigorous reaction set in, as reported by Smith and Rogier (68), but the greyish suspension suddenly changed into a white suspension 15 min. after addition of the hydride solution was complete. The mixture, cooled in an ice bath, was cautiously hydrolyzed with 10% sulfuric acid until acidic. The layers were separated, the aqueous solution was extracted with two 100-ml. portions of ether and the ethereal solution was dried over magnesium sulfate. The ether was separated by distillation through a 45-cm. Helipak packed column and the residue was distilled through a small distillation head with Vigreux indentations in the side arm. The main fraction, b.p. $95-98^{\circ}$, n_D^{25} 1.4264 (lit. (68,108,109) b.p. $97-101^{\circ}$; b.p. $99.3-99.5^{\circ}$ (771 mm.); b.p. $100-102^{\circ}$, n_D^{25} 1.4268-1.4281) amounted to 22.3 g. (47.1%) and was indicated to contain at least 98% of one component. The infrared spectrum of this material was identical in all respects with a spectrum of cyclopropanecarboxaldehyde which was prepared by Mazur (109) by the Oppenauer oxidation of cyclopropylcarbinol.

Cyclopropanecarboxaldehyde 2,4-dinitrophenylhydrazone was prepared and recrystallized from ethanol-ethyl acetate and had m.p. 182.6-183.7° (lit. (68, 110, 111) m.p. 185.5-186.5°; m.p. 182-185°; m.p. 185.0-186.5°).

1-Phenylcyclopropanecarbonitrile was prepared by the method of Knowles and Cloke (112) as amended by Case (113). Several runs were made by this procedure and the yield did not differ significantly from run to run. A suspension of sodamide in ether was prepared by the usual method from 46.0 g. (2.0 g. atom) sodium and 1500 ml. of liquid ammonia which was later replaced with 650 ml. of dry ether. To the well-stirred sodamide suspension in ether was added 117.0 g. (1.0 mole) of phenylacetonitrile at such a rate so as to maintain a gentle rate of reflux. The mixture was stirred and heated on a steam bath for 3 hr. To the cooled suspension was added a solution of 188 g. (1.0 mole) of ethylene dibromide in an equal volume of ether. The mixture was stirred and heated on a steam bath for 10 hr. at the end of which time there was only a slight evolution of ammonia. A total of 250 ml. of water was cautiously added to dissolve the salts which had formed during the reaction. The layers were separated and the aqueous solution was extracted with two 200-ml. portions of ether. The combined ethereal solutions were dried overnight over magnesium sulfate, the ether was distilled off on the steam bath and the residue was distilled in vacuo through a wire-spiral packed column to give 75.5 g. (52.8%) of 1-phenylcyclopropanecarbonitrile, b.p. 79-85° (0.5 mm.), n_D^{25} 1.5369 (lit. (112, 114, 115) b.p. 250-253° (761 mm.);

b.p. 125° (15 mm.), n_D^{20} 1.5382; n_D^{20} 1.5386). The infrared spectrum of this material was identical with that reported by Wiberley and Bunce (114). The earlier fractions from the distillation, amounting to 10.1 g., were principally composed of recovered phenylacetonitrile, identified by its infrared spectrum, and which is also a minor contaminant in the product. The nuclear magnetic resonance spectrum of 1-phenylcyclopropanecarbonitrile showed a single phenyl resonance and a symmetrical pattern characteristic of the methylene protons of a 1,1-disubstituted cyclopropane.

1-Phenylcyclopropanecarboxaldehyde. Several preparations of this compound were made of which the best procedure will be described. The procedure was adapted from that used in the preparation of cyclopropanecarboxaldehyde. A solution of lithium aluminum hydride in ether was prepared from 4.2 g. (0.11 mole) of lithium aluminum hydride and 250 ml. of dry ether and was filtered through a plug of glass wool before use. To a solution of 57.2 g. (0.4 mole) of 1-phenylcyclopropanecarbonitrile in 130 ml. of dry ether, cooled in a Dry Ice-acetone bath, was added the hydride solution dropwise with vigorous stirring over a period of 1 hr. Shortly after addition was complete, the greyish ethereal suspension suddenly changed to a brilliant white (and on one occasion a bright yellow) suspension. The mixture was stirred for 8 hr. as the temperature of the bath was gradually raised to 5°. The mixture was cautiously hydrolyzed with 10% sulfuric acid. The layers were separated and the aqueous acidic layer was extracted

with ether. The ethereal solution was dried over magnesium sulfate. The ether was removed by distillation through a 30-cm. Vigreux column and the residue was distilled through a 30-cm. wire-spiral packed column. There was collected 33.4 g. of material, b.p. 65-71° (1 mm.), n_D^{25} 1.5400-1.5404, identified as 1-phenylcyclopropanecarboxaldehyde by its infrared spectrum. The usual aldehyde C-H bands appeared at 2650 cm^{-1} , 2740 cm^{-1} and 2800 cm^{-1} , the carbonyl band was at 1707 cm^{-1} , the aromatic bands appeared at 1600 cm^{-1} , 1500 cm^{-1} and 690 cm^{-1} , and there was a band at 1025 cm^{-1} which is characteristic of cyclopropane compounds. The infrared spectra of some of the fractions had a band at 2250 cm^{-1} which is due to unreacted 1-phenylcyclopropanecarbonitrile. There was obtained 10.3 g. of a higher boiling fraction which was largely recovered 1-phenylcyclopropanecarbonitrile. The yield of aldehyde was 57.2% based on nitrile taken and 70% based on non-recovered nitrile. The nuclear magnetic resonance spectrum of 1-phenylcyclopropanecarboxaldehyde was similar to that described above for 1-phenylcyclopropanecarbonitrile.

An analytical sample of 1-phenylcyclopropane carboxaldehyde was prepared from some of the nitrile-containing fractions above by the following procedure. The material was dissolved in ethanol and treated with saturated sodium bisulfite solution. A crystalline solid formed which was shown not to be a bisulfite addition compound by its failure to regenerate aldehyde on treatment with saturated sodium bicarbonate solution. The aqueous-ethanolic bisulfite solution was

extracted several times with ether. The aqueous layer was made basic and was re-extracted with ether. After the ethereal solution had been dried and the ether was removed by distillation, the residue was distilled in vacuo through a 30-cm. wire-spiral packed column. The main fraction had b.p. 45.0-45.5° (0.5 mm.), n_D^{25} 1.5402.

Anal. Calcd. for $C_{10}H_{10}O$: C, 82.16; H, 6.90. Found: C, 82.12; H, 7.11.

The 2,4-dinitrophenylhydrazone was prepared and had m.p. 190.4-191.8° after three recrystallizations from ethanol-ethyl acetate.

Anal. Calcd. for $C_{16}H_{14}N_4O_4$: C, 58.89; H, 4.32. Found: C, 59.10; H, 4.45.

(1-Phenylcyclopropyl)-carbinylamine. The acidic aqueous solution obtained from the reduction of 1-phenylcyclopropanecarbonitrile after hydrolysis was made basic with sodium hydroxide solution and was extracted with ether. After the ethereal solution had been dried over sodium sulfate, the ether was distilled through a 45.-cm. Helipak packed column and the residue was distilled through a small distillation head with Vigreux indentations in the side arm. There was collected in several fractions 5.75 g. of (1-phenylcyclopropyl)-carbinylamine, identified by its infrared spectrum, having b.p. 103.0-108.5° (18.5 mm.), n_D^{25} 1.5385-1.5392. The yield of amine is 9.2% based on the initial quantity of 1-phenylcyclopropanecarbonitrile used in the reduction. The material obtained above was indicated to be pure by v-p-c.

Anal. Calcd. for $C_{10}H_{13}N$: C, 81.58; H, 8.90. Found: C, 81.46; H, 8.90.

An additional neutral compound was isolated in some of the above preparations. In one run, a fraction, 9.6 g., b.p. 60-164° (1 mm.) was redistilled to give 6.3 g. of material having b.p. 164-166° (0.5 mm.) n_D^{25} 1.5685, which formed a 2,4-dinitrophenylhydrazone of m.p. 189.0-190.6° after recrystallization from ethanol-ethyl acetate; a mixed m.p. with 1-phenylcyclopropanecarboxaldehyde was undepressed at 188.8-189.8°. The neutral compound did not have a carbonyl band in its infrared spectrum but it had a band of medium intensity at 1655 cm^{-1} . This band is undoubtedly due to $>C=N-$ absorption. The nuclear magnetic resonance spectrum of this material supported the imine structure; there was a resonance (strength 1) at slightly lower field than the phenyl resonance, a resonance (strength 2) in the region characteristic of methylene proton resonances and a resonance (strength 4) superimposed on a characteristically complex cyclopropane doublet. Based on this evidence, the compound was assigned the structure of the Schiff's base of 1-phenylcyclopropanecarboxaldehyde and (1-phenylcyclopropyl)-carbinylamine. A sample was redistilled for elemental analysis, b.p. 125-130° (0.4 mm.), n_D^{25} 1.5682.

Anal. Calcd. for $C_{20}H_{21}N$: C, 87.23; H, 7.69. Found: C, 87.08; H, 7.81.

3-Methyl-3-cyanopyrazoline was prepared by the method of Cox (116), as adapted from the procedure used by Siegel and Bergstrom (117) to prepare 1-methylcarbomethoxycyclopropane. N-nitroso-N-methylurea was prepared in large quantities by standard procedures(118). (Caution: In later preparations of N-nitroso-N-methylurea, the author developed a serious dermatitis on his hands. Care should be taken to prevent contact of this material with the skin.) Diazomethane was prepared by adding N-nitroso-N-methylurea to a magnetically stirred mixture of 50% potassium hydroxide solution and ether, cooled in an ice-salt bath. In a typical run, 68 g. (0.85 mole) of N-nitroso-N-methylurea was added to a mixture of 200 ml. of 50% potassium hydroxide solution and 350 ml. of ether. The bright-yellow ethereal layer was decanted and the aqueous solution was washed with two 100-ml. portions of ether. The combined ethereal solutions were dried over potassium hydroxide pellets. To the diazomethane solution, stirred mechanically (glass stirrer) and cooled in in an ice-salt bath was added dropwise 34 g. (0.5 mole) of methacrylonitrile (redistilled, b.p. 89.0-89.2° (744 mm.), n_D^{25} 1.3978) over a period of 1.5 hr. The mixture was stirred for 2 hr. and was then allowed to stand overnight. The ether was removed in vacuo (water aspirator) as the solution was heated in a water bath at 35°. A light-yellow residue of crude 3-methyl-3-cyanopyrazoline remained which amounted to 52 g. (95.5%).

1-Methylcyclopropanecarbonitrile. According to Cox's procedure (116), the pyrazoline is decomposed by heating small samples

in a large flask gently with a free flame. In all attempts to repeat this procedure, the reaction got out of control as the pyrazoline decomposed violently and much material was lost. A modification was therefore used in which the pyrazoline was first dissolved in redistilled anisole and the solution was heated in an oil bath. Batches of 20-30 g. of pyrazoline in 70-90 ml. of anisole were used in the decompositions. Gas evolution commenced at a bath temperature of 95° and proceeded smoothly at 100-110°. While vigorous, the reaction never got out of control. The reaction was completed by heating the mixture at 150°. The mixture was treated with alkaline potassium permanganate solution (116) to remove any olefinic products. The permanganate solution was added until its color persisted. The mixture was then extracted with five 100-ml. portions of petroleum ether and the combined extracts were dried over sodium sulfate. The bulk of the petroleum ether was removed by distillation through a Vigreux column (bath temperature 95°) and the residue was distilled slowly through a large spinning-band column operating at 1300 r.p.m. as the oil bath temperature was slowly raised. A Helipak packed column was previously found to be ineffective in separating 1-methylcyclopropanecarbonitrile and anisole. In a run starting with 1.0 mole of methacrylonitrile, there was obtained 39.8 g. (49.1%) of 1-methylcyclopropanecarbonitrile, b.p. 126.0-127.0°, n_D^{25} 1.4125 (Cox (116) reports b.p. 127.7-128.5°, n_D^{25} 1.4128; lit. (119) b.p. 127.0-127.5°, n_D^{20} 1.4141). The infrared spectrum of this material was identical with that obtained by Cox. The n-m-r spectrum

of 1-methylcyclopropanecarbonitrile showed a sharp singlet due to the methyl proton resonance followed at higher field by a symmetrical pattern characteristic of the ring protons of a 1,1-disubstituted cyclopropane.

1-Methylcyclopropanecarboxaldehyde was prepared several times from 1-methylcyclopropanecarbonitrile by the method described for the preparation of 1-phenylcyclopropanecarboxaldehyde (see above). In a typical run, 20 g. (0.25 mole) of 1-methylcyclopropanecarbonitrile and a solution prepared from 2.8 g. (0.074 mole) of lithium aluminum hydride afforded 15.9 g. (76.8%) of 1-methylcyclopropanecarboxaldehyde, b.p. 90-108°, n_D^{25} 1.4245-1.4251. The main fraction had b.p. 106-108°, n_D^{25} 1.4251, and was indicated to be at least 98% pure by v-p-c. The infrared spectrum of 1-methylcyclopropanecarboxaldehyde had a carbonyl band at 1710 cm^{-1} , aldehyde C-H bands at 2700 cm^{-1} and 2800 cm^{-1} and a cyclopropyl band at 1020 cm^{-1} . There were no bands attributable to olefinic unsaturation. The n-m-r spectrum showed a low-field resonance for the aldehyde proton and, at much higher field, a single sharp resonance for the methyl protons superimposed on a pattern typical of cyclopropyl ring-proton resonances. Some fractions were carefully redistilled through a 30-cm. wire-spiral column packed column to give material, b.p. 103.5-104.0°, n_D^{25} 1.4265, which showed only one peak in its vapor-phase-chromatogram. A satisfactory elemental analysis of this material was not obtained, however.

Anal. Calcd. for C_5H_8O : C, 71.39; H, 9.59. Found:

C, 69.32; H, 9.09.

A sample of 1-methylcyclopropanecarboxaldehyde which afforded a correct elemental analysis was prepared as follows. A sample of the purest aldehyde obtained above was dried over Drierite and distilled through a 30-cm. wire-spiral packed column in a nitrogen atmosphere. The fractions were collected in vials which could be directly sealed under nitrogen without further handling of the aldehyde. During all operations, air was scrupulously excluded. The analytical sample had b.p. $103-104^\circ$, n_D^{25} 1.4259.

Anal. Calcd. for C_5H_8O : C, 71.39; H, 9.59. Found:

C, 71.00, 70.91; H, 9.51, 9.40.

The observation that satisfactory analyses could not be obtained unless distillation was carried out in an inert, oxygen-free atmosphere suggests that the aldehyde was contaminated by up to 10% of peroxidized material formed on contact with air. Such compounds might not appear in the vapor-phase-chromatogram.

The 2,4-dinitrophenylhydrazone of 1-methylcyclopropanecarboxaldehyde was prepared and recrystallized from ethanol-ethyl acetate to give orange needles, m.p. $222.1-222.8^\circ$.

Anal. Calcd. for $C_{11}H_{12}N_4O_4$: C, 50.00; H, 4.58. Found:

C, 49.90; H, 4.80.

Zinc-Copper Couple. At the time that this work was done, a paper by Simmons and Smith (72) describing a new synthesis of

cyclopropanes had not been published (a preprint later became available) and the experimental procedure used here was based on the scant information available in an earlier published communication (120) and a private communication from Dr. Smith (121). Zinc dust and copper oxide, in proportions of 8:1, were thoroughly mixed and placed in quartz combustion boats and heated in a quartz tube with a muffle furnace. The tube was fitted with a gas inlet and outlet and a thermocouple wire which dipped into the metal in one of the boats. Hydrogen, dried by passage through sulfuric acid, was passed through the tube at 40-50 ml./min. The temperature in the tube, according to the thermocouple reading, was gradually raised to 500° over a period of 4 hr. and maintained at 500° for 30 min.; it was then allowed to fall to room temperature. A grey powder resulted which was either used immediately or stored in a tightly sealed bottle. It is reported (72) that the couple remains active on storage. Some shiny pellets occasionally formed which are reported to be unreactive (72) and so were manually separated from the grey powder. In some earlier runs, prior to the communication from Dr. Smith (121), the metallic mixture was simply placed in a quartz tube which was gradually heated to 500-550°. The couple so prepared was found to be active on subsequent use, but it is not known whether such material is more or less active than the couple prepared by the later procedure.

Bicyclo[4.1.0]heptane was prepared from cyclohexene by the method of Simmons and Smith (72) as a test of the procedure. To a

mixture of 24.6 g. (0.3 mole) of cyclohexene and 40.2 g. (0.15 mole) of redistilled methylene iodide in 50 ml. of ether was added 18 g. (0.25 g. atom zinc) of the zinc-copper couple. The mixture was stirred magnetically at reflux for 48 hr. The mixture was filtered and distilled directly through a distillation head to give a series of fractions totaling 17.5 g., b.p. 53-104°, which were shown by v-p-c to be mixtures of cyclohexene (about 60%) and a higher boiling component, presumably bicyclo[4.1.0]heptane. The yield of the latter, according to v-p-c, was about 50%. Simmons and Smith (72) report a 48% yield of bicyclo[4.1.0]heptane, b.p. 116.5°, n_D^{25} 1.4546. The crude material obtained in the present experiment was redistilled through a spinning-band column to give 3.2 g. (22.4%) of material, b.p. 113-115°, n_D^{25} 1.4548. The total amount of material recovered from the distillation amounted to only 9.0 g. because there was a leak in the column. The corrected yield of pure bicyclo[4.1.0]heptane is about 40%, in agreement with the yield based upon analysis of the crude reaction product by v-p-c. The infrared spectrum of the product, clearly that of a hydrocarbon, showed no absorption in the regions characteristic of olefinic unsaturation.

Phenylcyclopropane from Styrene. The Simmons-Smith reaction (72) was run as above with 40.2 g. (0.15 mole) of methylene iodide, 31.2 g. (0.30 mole) of styrene and 15.7 g. (0.22 g. atom zinc) in 200 ml. of dry ether. The product was distilled to give 11.5 g., b.p. 50-58° (16 mm.), which was indicated by v-p-c to be a mixture of about 80% methylene iodide and 20% of another material which is not

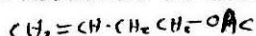
recovered styrene and is undoubtedly phenylcyclopropane. All attempts at separating the two components by distillation or by reaction with active metals failed completely. Simmons (121) has reported that methylene iodide and phenylcyclopropane can only be separated by preparative v-p-c.

Cyclopropylacetonitrile from Allyl Cyanide (Attempted). Cuprous cyanide and allyl cyanide were prepared by the standard procedures (122, 56). The yield of allyl cyanide was consistently 91-92% and the product was indicated to be at least 99% pure by v-p-c. After treatment of allylcyanide with methylene iodide and zinc-copper couple in ether, as above, the reaction mixture became extremely viscous and dark in a few hours. Since no low-boiling distillable material could be isolated, the mixture was not further investigated.

Allylcarbinol was prepared by the reduction of 68 g. (0.79 mole) of redistilled vinylacetic acid (122a) with 27 g. (0.71 mole) of lithium aluminum hydride in ether by standard procedures. The mixture was carefully hydrolyzed with 10% sulfuric acid and extracted several times with ether. After being dried, the ethereal solution was distilled to give 37.9 g. (66.7%) of allylcarbinol, b.p. 109-112°, n_D^{25} 1.4190 (lit. (38, 123) b.p. 115° (770 mm.), n_D^{25} 1.4182; b.p. 112-113.5°, n_D^{20} 1.4224).

2-Cyclopropylethanol from Allylcarbinol (Attempted). Allylcarbinol, methylene iodide and zinc-copper couple were mixed in ether as above. The mixture spontaneously warmed to reflux and was magnetically stirred at reflux for 60 hr. Filtration and distillation of the

filtrate gave a small amount of distillate and mostly tars. The distillate was analyzed by v-p-c and was shown to consist of about a dozen components of which the main component (about 70%) was recovered allylcarbinol. Work was discontinued on this reaction.



Allylcarbiny Acetate. In a 500-ml. three-necked flask, equipped with a mechanical stirrer, thermometer and dropping funnel, was placed 36.8 g. (0.51 mole) of allylcarbinol dissolved in 150 ml. of 2,4,6-collidine. The mixture was cooled to -5° in an ice-salt bath and 50 g. (0.64 mole) of acetyl chloride was slowly added over a period of 2 hr. as the temperature was kept below 0° . After the mixture had been stirred for an additional 2.5 hr., 150 ml. of 10% sulfuric acid followed by 100 ml. of chloroform was added. The aqueous layer was extracted with chloroform and the combined chloroform extracts were washed with acid and water and then dried over magnesium sulfate. The solution was distilled through a 45-cm. Helipak packed column. The main fraction collected was 31.6 g., b.p. $121-123^\circ$, n_D^{25} 1.4104 (lit. (43b, 124) b.p. 127° , n_D^{25} 1.4066-1.4070; b.p. 126° , n_D^{20} 1.4105). This fraction was indicated to be at least 90% pure by v-p-c. The total amount of material collected of apparently 96% purity was 38.3 g. (66.0%), b.p. $119-123^\circ$. The infrared spectrum of this material was identical to that reported for allylcarbiny acetate by Roberts and Chambers (43b).

2-Cyclopropylethyl Acetate from Allylcarbiny Acetate. The Simmons-Smith reaction was carried out as before with 11.4 g. (0.1 mole) of allylcarbiny acetate, 53.6 g. (0.2 mole) of methylene iodide

and 17.7 g. (0.25 g. atom zinc) of the zinc-copper couple in 75 ml. of dry ether. After being stirred at reflux for 60 hr., the mixture was filtered and the filtrate was distilled. The residue, after removal of the ether, was distilled in vacuo to reduce the chance of ester pyrolysis, which occurred in an earlier run. There was collected 12.2 g. of material, b.p. 30° (57.5 mm.) to 70° (22 mm.). This material was shown to be a mixture of several components by v-p-c, including some recovered allylcarbinyl acetate. Redistillation through a spinning-band column was not effective at completely separating the components, according to the v-p-c analyses of the distillate. The best fraction, 2.7 g., b.p. 146°, was shown by v-p-c to consist mainly of one component (about 90% purity) which is most probably 2-cyclopropylethyl acetate, according to its infrared spectrum (see below). Based on the v-p-c analyses, it was estimated that the total crude yield of 2-cyclopropylethyl acetate is about 3 g. (23%), while about 3.5 g. of allylcarbinyl acetate was recovered. The fractions of b.p. 120-146° were treated with alkaline potassium permanganate as described above in the purification of 1-methylcyclopropanecarbonitrile. The resulting mixture was extracted with ether and the ethereal solution was dried over magnesium sulfate. Ether was distilled through a 30-cm. glass helices packed column and the residue was distilled through a spinning-band column with decalin used as a still base. There was obtained 1.06 g. of 2-cyclopropylethyl acetate, n_D^{25} 1.4200, which was indicated to be

at least 98% pure, according to v-p-c. The overall yield of the pure cyclic ester was 8.3%. The infrared spectrum of 2-cyclopropylethyl acetate was strikingly similar to that of allylcarbinyl acetate except that the bands due to olefinic unsaturation at 1645 cm^{-1} , 988 cm^{-1} and 915 cm^{-1} are absent and a new band is present at 1016 cm^{-1} (cyclopropyl absorption band) with weak bands at 960 cm^{-1} and 915 cm^{-1} . The carbonyl band in both spectra was at 1740 cm^{-1} . The similarity in spectra is good evidence that the product is related to the starting material simply by transformation of a double bond to a cyclopropane ring.

3-Butenal Dimethyl Acetal. Several procedures for the preparation of 3-butenal dimethyl acetal and of the corresponding diethyl acetal were investigated. The best procedure will be described in detail for 3-butenal dimethyl acetal. Allylmagnesium bromide was prepared by the method of Young, Prater and Winstein (125). In a dry flask equipped with an efficient mechanical stirrer, a reflux condenser and a dropping funnel was placed 13.0 g. (5.4 g. atom) magnesium and 600 ml. anhydrous ether. The mixture was stirred vigorously in a nitrogen atmosphere and to it was slowly added 98 g. (0.81 mole) of redistilled allyl bromide (b.p. $68.0-68.5^\circ$) in ether over the course of 6 hr. A 10-ml. aliquot of the Grignard solution was titrated by the method of Gilman, Zoellner and Dickey (126). The aliquot was added to an excess of standard acid, the mixture was heated on a hot plate

for 15 min. and the excess acid was back-titrated with standard base to a phenolphthalein end-point. The concentration of the Grignard solution was found to be 0.950 N and 0.952 N in two determinations. The total mixture was filtered through a glass wool plug under nitrogen pressure into a graduated separatory funnel. The Grignard solution amounted to 675 ml., corresponding to 0.64 moles (79%) of allylmagnesium bromide. The Grignard reagent was transferred into a fresh dry flask equipped as above and was heated to reflux. To the solution was added a solution of 50.9 g. (0.48 mole) of redistilled methyl orthoformate, b.p. 99-100°, in 200 ml. of dry ether over a period of one hour. At this time a sample of the reaction mixture gave a strongly positive Gilman color test indicating the presence of Grignard reagent(127). Stirring and heating were continued for a total of 39 hr. At the end of this time, a sample of the reaction mixture still gave a positive Gilman color test (127) for the presence of Grignard reagent. A small sample was hydrolyzed and analyzed by v-p-c and was shown to contain only a small amount of methyl orthoformate. On slowly pouring the reaction mixture over crushed ice, vigorous gas evolution took place. The ethereal layer was decanted and the gelatinous water layer was stirred with three fresh portions of ether. The combined ethereal solutions were dried over potassium carbonate. Ether was removed by distillation through a 55-cm. Helipak packed column and the residue was distilled through a 30-cm. wire-spiral packed column to give 23.7 g., b.p. 108-112°. This material was indicated by v-p-c to contain only small

amounts of residual orthoformic ester and at least 90% of a new component, presumably 3-butenal dimethyl acetal. On redistillation through a spinning-band column a series of fractions were obtained totaling 16.9 g., b.p. 109-112°, which, according to v-p-c, consisted of 97-99% of one component. The yield of pure 3-butenal dimethyl acetal was 30.4% of theory. The infrared spectrum supported the structural assignment; there was no carbonyl band whereas bands characteristic of olefinic unsaturation appeared at 1645 cm^{-1} , 985 cm^{-1} and 915 cm^{-1} and broad bands in the region $1000\text{-}1200\text{ cm}^{-1}$ suggested ether linkages.

3-Butenal Diethyl Acetal. The same procedure was used in the preparation of 3-butenal diethyl acetal as described above for the dimethyl acetal, except that redistilled ethyl orthoformate (b.p. 143-144° (746 mm.), n_D^{25} 1.3889) was used in place of methyl orthoformate. In all runs, the mixture boiled at 142-143° and consisted of approximately 75% 3-butenal diethyl acetal and 25% ethyl orthoformate, according to v-p-c. Further separation of the components was not attempted.

A 2,4-dinitrophenylhydrazone was prepared by treating the acetal mixture above with the standard ethanol-sulfuric acid solution of 2,4-dinitrophenylhydrazine. A derivative was isolated and recrystallized from ethanol-ethyl acetate, m.p. 186.2-187.1°. A sample of crotonaldehyde 2,4-dinitrophenylhydrazone was prepared and recrystallized from ethanol-ethyl acetate, m.p. 185.6-187.5°; mixed melting point of the two hydrazones was 186.0-187.8°. To avoid acid-catalyzed

isomerization of the unconjugated derivative to the conjugated isomer, the 2,4-dinitrophenylhydrazone was prepared by the method of Roberts (128). In 13 ml. of 80% ethanol was dissolved 0.5 g. of 2,4-dinitrophenylhydrazine and 1 drop of conc. hydrochloric acid. To this was added 3 ml. of the crude acetal above and the mixture was heated to boiling. Filtration and repeated recrystallization afforded light orange plates with a reproducible m.p. of 121.9-122.8°. This material did not give a satisfactory analysis.

Anal. Calcd. for $C_{10}H_{10}N_4O_4$: C, 48.00; H, 4.03. Found: C, 45.99; H, 4.15.

The only previous mention of 3-butenal in the literature is by Farberov and Ustavshchikov (129) who reported an aldehyde of b.p. 90-100°, 2,4-dinitrophenylhydrazone m.p. 164°, to which they assigned the structure 3-butenal without any further evidence.

3-Methyl-3-butenal Diethyl Acetal. The procedure described above for the preparation of 3-butenal dimethyl acetal was repeated using 48 g. (2.0 g. atom) of magnesium turnings, 45.2 g. (0.50 mole) of redistilled methallyl chloride (b.p. 69.5-71.0°, n_D^{25} 1.4243) and 60 g. (0.40 mole) of redistilled ethyl orthoformate. There was obtained 46.2 g., b.p. 120-148°. Analysis by v-p-c showed the presence of recovered ethyl orthoformate and a new component, presumably 3-methyl-3-butenal diethyl acetal. Redistillation through a spinning-band column afforded a series of fractions amounting to 7.8 g., b.p. 153-158°, which were indicated by v-p-c to be rich in the new component to the extent of

about 95%. The yield of 3-methyl-3-butenal diethyl acetal was 22.6% based on non-recovered ethyl orthoformate. The infrared spectrum of the product was similar to that described above for 3-butenal dimethyl acetal except that there was a very strong band at 888 cm^{-1} with shoulders at 925 cm^{-1} and 990 cm^{-1} .

3-Methyl-3-butenal Dimethyl Acetal was prepared as described for 3-butenal dimethyl acetal from 144 g. (6.0 g. atom) of magnesium turnings, 90.5 g. (1.0 mole) of redistilled methallyl chloride and 30 g. (0.28 mole) of redistilled methyl orthoformate. The yield of Grignard reagent was quite low due to the formation of precipitates which made transference and filtration of the Grignard solution, as described above, difficult. The progress of the reaction of the Grignard reagent with the orthoformate was followed by Gilman tests (127) and by v-p-c analysis after hydrolysis. The Gilman test was still positive and there was unreacted methyl orthoformate present after the mixture had been stirred and heated at reflux for five days. The mixture was hydrolyzed, extracted and distilled as for 3-butenal dimethyl acetal, and there was obtained 14.7 g. (40.4%) of 3-methyl-3-butenal dimethyl acetal, b.p. $128.5-130.0^\circ$, n_D^{25} 1.4132. The n-m-r spectrum of this compound showed a low field resonance (strength 2) for the vinyl protons and the expected resonances at higher field for the tertiary acetal proton, the methoxy protons, the methylene protons and the protons on the methyl group, all in complete accord with the assigned structure.

Anal. Calc. for $C_7H_{14}O_2$: C, 64.58; H, 10.84. Found:

C, 64.56; H, 10.86.

Cyclopropylacetaldehyde Diethyl Acetal from 3-Butenal Diethyl Acetal (Attempted). The Simmons-Smith reaction, as described above in the preparation of bicyclo[4.1.0]heptane, was run three times with the mixture of 3-butenal diethyl acetal and ethyl orthoformate described above. In all runs, the reaction mixture became very dark after a short time. In one run, the mixture was treated with acid and, in another, with base before distillation in order to remove zinc iodide from the ethereal solution. In the third run, the residue, after centrifugation to remove the residual metals, was distilled directly. In all runs, only small amounts of material were obtained as the bulk of the material formed tars. Analysis of the distillate by v-p-c indicated the presence of a great many components. These complex mixtures were not studied further.

Cyclopropylacetaldehyde Dimethyl Acetal from 3-Butenal Dimethyl Acetal (Attempted). The Simmons-Smith reaction was run as described above for the preparation of bicyclo[4.1.0]heptane. A modification was used in that a few crystals of iodine were added to the couple in ether and the mixture was stirred until the iodine color disappeared before methylene iodide and 3-butenal dimethyl acetal were added. After being stirred at reflux for 48 hr., the mixture was centrifuged to remove residual metal and the centrifugate was washed with cold 10% ammonium chloride solution, dilute ammonium hydroxide

solution and was dried over magnesium sulfate. Removal of the ether by distillation left a small dark residue. Only 0.8 g. of a very complex mixture, according to v-p-c, was obtained before the residue changed into a solid black undistillable tar.

In another run, the reaction was followed by analyzing samples by v-p-c after they had been treated as above. Although very little 3-butenal dimethyl acetal was consumed over a period of 20 hr., all the methylene iodide had been consumed. No new components in appreciable quantities appeared in the vapor phase chromatogram. Fresh methylene iodide was added to the mixture and, after a total of 34 hr., all the peaks due to the starting materials were absent from the chromatogram. Treatment of the rest of the mixture as described above and distillation gave only 0.2 g. of a serious mixture of compounds, according to v-p-c, and tars.

In a final run of this reaction in which cyclohexane was used to calibrate the vapor phase chromatogram, it was found that 3-butenal dimethyl acetal was gradually consumed, although no appreciable quantity of new components appeared in the chromatogram. As a test of the activity of the above reagents, samples of the same batches of methylene iodide and zinc-copper couple were reacted with cyclohexene in ether. The reaction was followed by v-p-c and it was seen that one new component appeared in the chromatogram. The area of the peak due to this new component, which had the same retention time as bicyclo[4.1.0]heptane obtained previously, grew to twice the area of

the cyclohexene peak after 30 hours and to four times the area of the cyclohexene peak after 48 hours. This experiment confirms the reactivity of the methylene iodide and zinc-copper couple which were ineffective in reaction with 3-butenal dimethyl acetal.

(1-Methylcyclopropyl)-acetaldehyde Dimethyl and Diethyl Acetals

(Attempted). All attempts at the Simmons-Smith reaction using 3-methyl-3-butenal dimethyl and diethyl acetal met with the same lack of success encountered with the 3-butenal acetals. Again, only small quantities of distillable material were isolated before the bulk of the material turned to tar. The distillates consisted of many components including recovered starting materials and were not investigated further.

Methyl Cyclopropylacetate. Cyclopropanecarbonyl chloride, b.p. 115-117°, prepared by the reaction of thionyl chloride and cyclopropanecarboxylic acid. A solution of diazomethane in ether was prepared from 0.75 mole of N-nitroso-N-methylurea by the procedure described earlier (see page 90). To the diazomethane solution, in a 1-liter three-necked flask equipped with a magnetic stirrer and cooled in an ice-salt bath, was slowly added 26 g. (0.25 mole) of cyclopropanecarbonyl chloride in 75 ml. of ether. The mixture, which became cloudy almost immediately, was stirred for 30 min. with cooling and for 3 hr. at room temperature. The ether was removed in vacuo (water aspirator) as the flask was heated in a water bath at 30°, leaving a yellow residue of diazoketone.

The Wolff rearrangement of the diazoketone was accomplished by means of the Newman modification (74). Silver benzoate was prepared

from solutions of sodium benzoate and silver acetate and was dried for two days in a vacuum oven at 80° and 1 mm. Trimethylamine was dried over sodium. Silver benzoate was dissolved in triethylamine and the solution was filtered before use to remove undissolved solids. The crude diazoketone above was dissolved in 400 ml. of methanol and the silver benzoate solution was added in small portions. New portions were added whenever gas evolution abated. A total of 17 g. of silver benzoate in 170 ml. of triethylamine was used as 86% of the theoretical amount of nitrogen was collected. The mixture was stirred at room temperature for 36 hr. Charcoal was added to the mixture after it had been heated to reflux and the hot mixture was filtered. Methanol and most of the triethylamine were removed by distillation through a 30-cm. column packed with glass helices. The residue was dissolved in 150 ml. of ether and the column was washed with 50 ml. of ether. The ethereal solution was washed with 150- and 100-ml. portions of 15% sodium carbonate, two 50-ml. portions of water and three portions of 3N hydrochloric acid. The ethereal solution was dried over magnesium sulfate. The ether was removed by distillation through a 30-cm. column packed with glass helices and the residue was distilled through a distillation head with Vigreux indentations in the side arm to give 9.87 g., b.p. 126-120°, n_D^{25} 1.4180. Smith and McKenzie (75) prepared methyl cyclopropylacetate by esterification of cyclopropaneacetic acid and reported b.p. 132°, n_D^{23} 1.4175. The infrared spectrum of the compound obtained by the above method has a carbonyl band at 1742 cm^{-1} , a cyclopropyl band at 1010 cm^{-1} and no absorptions characteristic of olefinic

unsaturation. Based on this evidence and the general agreement with Smith and McKenzie's data, the product was assumed to be methyl cyclopropylacetate. The yield was 34.6%.

2-Cyclopropylethanol. To 2.0 g. (0.05 mole) of lithium aluminum hydride in 150 ml. of dry ether, cooled in an ice bath and stirred mechanically, was added dropwise a solution of 8.9 g. (0.078 mole) of methyl cyclopropylacetate in 50 ml. of dry ether over the course of 2 hr. The mixture was stirred at room temperature for 30 min. and for 6 hr., and was then allowed to stand overnight. Very careful hydrolysis with 10 ml. of water was followed by addition of 10% sulfuric acid until the mixture was acidic. The layers were separated and the acid solution was extracted with ether. After the ethereal solution had been dried over sodium sulfate, the mixture was distilled to give 3.5 g., b.p. 134-139°, n_D^{25} 1.4322. Redistillation through a spinning-band column gave material, n_D^{25} 1.4321, which was indicated to be at least 98% pure, according to v-p-c. Hart and Wyman (40) report 2-cyclopropylethanol b.p. 135°, n_D^{25} 1.4327. A correct elementary analysis of the alcohol was not obtained.

Anal. Calcd. for $C_5H_{10}O$: C, 69.72; H, 11.70. Found: C, 67.62; H, 11.67.

The infrared spectrum of the alcohol supported the structure of 2-cyclopropylmethanol, but was not in itself diagnostic. However, the n-m-r spectrum substantiated the proposed structure. The unsplit hydroxyl resonance was followed, at increasing field strength,

by a cleanly separated triplet (strength 2) and a quartet (strength 2) for the alpha and beta methylene resonances, and by the usual complex pattern for the five cyclopropyl ring-protons at still higher field strength.

The 3,5-dinitrobenzoate of 2-cyclopropylethanol was prepared and recrystallized from ethanol-water, m.p. 61.0-63.0°.

Anal. Calcd. for $C_{12}H_{12}N_2O_6$: C, 51.43; H, 4.32. Found: C, 50.73; H, 4.15.

2-Cyclopropylethanol from Cyclopropyl Chloride (Attempted).

The following experiments were carried out before those described immediately above and were based on a private communication from Prof. H. Hart (73). Cyclopropylmagnesium chloride was prepared from cyclopropyl chloride and magnesium in purified tetrahydrofuran by entrainment with ethyl bromide. Iodine was added to promote formation of the Grignard reagent. The mixture was stirred for 19 hr. at reflux. A solution of ethylene oxide in tetrahydrofuran was added to the cooled Grignard solution and the mixture was stirred for 1 hr. at room temperature and 1 hr. at reflux. The mixture was poured over crushed ice and cold 6N hydrochloric acid was added to dissolve the inorganic salts. The solution was saturated with sodium chloride and extracted with ether. After being dried over magnesium sulfate, the solution was distilled to give 14.9 g., b.p. 70-120°. Redistillation afforded 9.8 g., b.p. 123-126°, of a mixture of n-butyl alcohol and

a new component, according to v-p-c. Very slow distillation of this mixture through a spinning-band column gave 6.3 g. of material of at least 99% purity, according to v-p-c, which had n_D^{25} 1.4386. This alcohol did not react with potassium permanganate solution and had a different spectrum and v-p-c retention time from 2-cyclopropylethanol as obtained previously by the reduction of methyl cyclopropylacetate. It was found later that this alcohol gave a positive Beilstein test(130) for halogen and its n-m-r spectrum showed only two types of proton resonances with an area ratio of 4:1. This is strong evidence that the alcohol obtained from the Grignard reaction was ethylene chlorohydrin (lit. (131a) b.p. 128.6°, n_D^{20} 1.4419).

Anal. Calcd. for C_2H_5ClO : C, 29.83; H, 6.26. Found: C, 30.68; H, 6.44.

The 3,5-dinitrobenzoate was prepared from the alcohol and 3,5-dinitrobenzoyl chloride and had m.p. 91.9-92.6° after several recrystallizations from ethanol (lit. (131b) m.p. 92° for ethylene chlorohydrin 3,5-dinitrobenzoate).

Anal. Calcd. for $C_9H_7N_2O_6Cl$: C, 39.36; H, 2.57; Cl, 12.91; N, 10.20. Found: C, 39.08; H, 5.41; Cl, 12.85; N, 9.72.

N,N-Dimethylcyclopropylacetamide. Several procedures for the synthesis of N,N-dimethylcyclopropylacetamide by the Arndt-Eistert reaction were investigated and the best procedure found will be described in detail. Diazoacetylcyclopropane was prepared from 47 g. (0.45 mole)

of cyclopropanecarbonyl chloride and diazomethane (generated from 90.6 g. (0.88 mole) of N-nitroso-N-methylurea) by a slight modification of the procedure described above in the synthesis of methyl cyclopropylacetate. According to the procedure of Newman and Beal (132), the diazoketone was prepared by adding the acid chloride to an ice-cooled solution of diazomethane and 45 g. (0.44 mole) of triethylamine in ether over a period of 4 hr. Theoretically, there should be no gas evolution by this method, but 0.15 mole of nitrogen was collected.* The mixture was stirred for 2 hr. at room temperature and 58 g. (96%) of triethylamine hydrochloride was then separated by filtration. The ether and excess diazomethane were removed in vacuo as before. The residual diazoketone was dissolved in 300 ml. of purified dioxane in a three-necked flask equipped with a magnetic stirrer, a Dry-Ice condenser from which tubing led to a gas measuring apparatus, a dropping funnel for adding 10% silver nitrate solution and a tube for bubbling in dimethylamine. The mixture was warmed to 50° whereupon the silver nitrate solution (200 ml.) and dimethylamine (100 g.) were added in small portions simultaneously. The mixture became very dark as soon as the addition was commenced. After 3.5 hr., 102% of the theoretical amount of nitrogen had been collected. The mixture was stirred and heated overnight. Filtration afforded a black residue of silver and a yellow filtrate which was distilled in vacuo to remove most of the solvent and

*Newman and Beal (132) also observed gas evolution when diazoketones were prepared from aliphatic but not aromatic acid chlorides.

and residual amine. The residue was treated with 3 N hydrochloric acid until the mixture was acidic. There was no gas evolution on acidification indicating that the diazoketone had been decomposed completely. The solution was extracted with chloroform and the chloroform extracts were dried over magnesium sulfate. The chloroform was removed by distillation on a steam bath and the residue was distilled in vacuo, b. p. 35-125° (33 mm.). Redistillation through a 30-cm. wire-spiral packed column afforded 30.79 g. (53.9%) of N,N-dimethylcyclopropylacetamide, b. p. 116-120° (30.5 mm.), n_D^{25} 1.4664. The infrared spectrum of this compound showed a band at 1660 cm^{-1} , characteristic of tertiary amides, and a cyclopropyl band at 1020 cm^{-1} . There is no absorption characteristic of olefins, alcohols, amines or other carbonyl compounds. The n-m-r spectrum gave evidence which supports the structure of the product as N,N-dimethylcyclopropylacetamide. There was a doublet at low field (strength 6) for the two N-methyl groups, which are not equivalent due to hindered rotation (133), followed by a doublet (strength 2) for the protons on the methylene group, split by coupling with the adjacent tertiary proton. The tertiary proton appeared as a highly split multiplet and there was a typically complex pattern for the other four ring protons. Some of the fractions obtained above were sufficiently pure, according to y-p-c analysis, to be submitted directly for elemental analysis.

Anal. Calcd. for $C_7H_{13}NO$: C, 66.10; H, 10.30. Found: C, 66.02; H, 10.31.

In some of the runs of the above synthesis, lower-boiling fractions were obtained, b.p. 74-115° (42 mm.), which gave positive tests with 2,4-dinitrophenylhydrazine reagent. The infrared spectra of these fractions showed a strong ketone carbonyl band at 1710 cm^{-1} as well as the 1025 cm^{-1} cyclopropyl band. They probably contained chloromethyl cyclopropyl ketone produced by reaction of hydrochloric acid and some unreacted diazoacetylcyclopropane. A 2,4-dinitrophenylhydrazone was prepared and recrystallized from ethanol and had m.p. 119.2-120.0°.

Anal. Calcd. for $C_{11}H_{11}N_4O_4Cl$: C, 44.23; H, 3.70; Cl, 11.87. Found: C, 44.06; H, 3.92; Cl, 11.89.

Cyclopropylacetaldehyde I. Reduction of N,N-Dimethylcyclopropylacetamide. A total of eleven runs were made of this reaction, based on the recently reported method of Brown and Tsukamoto (70), in an attempt to develop a procedure which could be used on a preparative scale. These attempts were unsuccessful. In all runs, a lithium aluminum hydride solution (approximately 1M) was prepared by stirring a slight excess of the reagent with ether for a few hours and then allowing the mixture to stand in order for the insoluble matter to settle. An aliquot of the clear solution was titrated iodimetrically by the standard procedure (134). Duplicate titrations agreed to within a few percent. Measured volumes of the standardized solutions were used in the following way. To the hydride solution, magnetically stirred

and cooled in an ice bath, was added a solution of an equimolar amount of ethyl acetate in ether. The suspension of lithium diethoxyaluminumhydride, in 15-25% excess, was then added to a cooled solution of N,N-dimethylcyclopropylacetamide (3 to 5 g. per run) in ether. The exact temperature and length of time of the reaction varied from run to run. In all cases, the reaction mixture was hydrolyzed after a few hours with 2N sulfuric acid which was added until the point was reached when the clear ether solution could be decanted from the gelatinous solid which adhered to the walls of the flask. In some runs, the gelatinous solid was dissolved in excess acid and this solution was extracted with ether. The extracts were added to the decanted ethereal solution which was then dried over sodium sulfate.

In one run, the ethereal solution was treated directly with excess 2,4-dinitrophenylhydrazine reagent. There was collected 2.5 g. of crude hydrazone (theoretical amount was 2.1 g.). Recrystallization from ethanol afforded 0.8 g. (38%) of cyclopropylacetaldehyde 2,4-dinitrophenylhydrazone, m.p. 141.5-143.0°.

Anal. Calcd. for $C_{11}H_{12}N_4O_4$: C, 50.00; H, 4.58. Found: C, 50.18; H, 4.88.

In several runs, the ether was removed by distillation through an efficient column and the residue was distilled through a small distillation head or center-rod column. In all cases, only small amounts of distillate were obtained and these consisted mainly of ethanol. Traces of higher-boiling fractions were obtained and these were indicated to be

complex mixtures of many components by v-p-c. Since samples of these fractions gave positive tests with 2,4-dinitrophenylhydrazine reagent, it was known that some aldehyde was present. Attempts were made to separate the aldehyde from the other components by treatment with sodium bisulfite solution. Decomposition of the bisulfite extracts in acid and base, extraction with ether, drying and distillation gave only very small amounts of impure aldehyde-containing material.

A somewhat better procedure was found in which the aldehyde was isolated directly as its semicarbazone. A paste was made from semicarbazide hydrochloride and sodium acetate by mixing in a mortar and pestle. Ethanol was added and the mixture was filtered to remove sodium chloride. The filtrate was added to the ethereal solution from the reduction and the mixture was stirred overnight. The solvents were removed using a water aspirator leaving an oil which crystallized on cooling. The yield of crude cyclopropylacetaldehyde semicarbazone was 66%. The solid was recrystallized from water several times; after being dried overnight in vacuo (1 mm.) at 55°, it had m. p. 140.8-142.2°.

Anal. Calcd. for $C_6H_{11}N_3O$: C, 51.04; H, 7.85; N, 29.77.

Found: C, 51.30, 51.49; H, 8.02, 8.13; N, 29.90, 30.00.

The most satisfactory procedure found for decomposition of the semicarbazone was that of Tiemann (135). The semicarbazone (4 g.) was heated with an approximately equimolar amount of phthalic anhydride (9.5 g.) in a flask equipped for steam distillation. The cloudy distillate

gave a positive test with 2,4-dinitrophenylhydrazine reagent. Approximately 750 ml. of distillate was collected in one run before the test for aldehyde became negligible. The distillate was saturated with sodium chloride and extracted with ether. The ethereal solution was dried over magnesium sulfate and the ether was removed by distillation through a 30-cm. column packed with glass helices. The small residue was distilled through a small distillation head to give 1.1 g. of cyclopropylacetaldehyde (18.6% based on N,N-dimethylcyclopropylacetamide), b.p. 98.0-105.5°, n_D^{25} 1.4172. The infrared spectrum of this material had the usual aldehyde C-H and carbonyl bands at 2700 cm^{-1} and 1745 cm^{-1} , respectively, cyclopropyl bands at 1020 cm^{-1} and 3080 cm^{-1} and no bands due to olefinic unsaturation. Cyclopropylacetaldehyde has been reported by Hart and Wyman (40) to have b.p. 105-106°, n_D^{25} 1.4382.*

In two runs, N,N-dimethylcyclopropylacetamide was reduced directly with lithium aluminum hydride. The hydride solution was slowly added to a solution of the amide cooled in an ice bath and the mixture was stirred for 1 hr. in the ice bath. The mixture was hydrolyzed, extracted, dried and distilled as above. There was obtained a 10-25% yield of cyclopropylacetaldehyde, b.p. 95-104°, n_D^{25} 1.4208. Analysis of the distillation fractions by v-p-c indicated that they consisted of about 95% cyclopropylacetaldehyde.

*The index of refraction as reported by Hart and Wyman (40) was in error. Prof. Hart (73) informs us the experimental value was actually n_D^{25} 1.4238.

Since sizeable quantities of cyclopropylacetaldehyde were needed for other experiments, the poor yields obtained in these experiments and the difficulties encountered in separating cyclopropylacetaldehyde from ethanol and the other organic compounds present in the reaction mixture made it impractical to pursue this method of synthesis.

Cyclopropylcarbinol. Cyclopropanecarboxylic acid and its precursor, γ -chlorobutyronitrile, were prepared several times according to standard procedures (136, 137) with the modifications made by White (79). Typical yields were 60.4% and 84.7% for the two steps, respectively. Cyclopropanecarboxylic acid used in later work was obtained commercially from Columbia Chemicals Corporation. Cyclopropylcarbinol was prepared many times by the reduction of cyclopropanecarboxylic acid with lithium aluminum hydride, according to standard procedures. In a typical run, 100 g. (2.63 mole) of lithium aluminum hydride and 200 g. (2.33 mole) of cyclopropanecarboxylic acid in ether afforded 132.5 g. (79.1%) of cyclopropylcarbinol, b.p. 120-123°, n_D^{25} 1.4301 (lit.(38)b.p.123°, n_D^{25} 1.4300). Yields as high as 82% were obtained in some runs. The best procedure for hydrolysis of the lithium-alcoholate complex was one in which 10% sulfuric acid was added to the reaction mixture until the white gelatinous precipitate which formed adhered to the walls of the flask; the clear ethereal solution could then be decanted from the solid. Additional small amounts of cyclopropylcarbinol could be obtained by treatment of the solid with

excess acid and extraction of the acidic solution, preferably continuously, with ether. Analysis by v-p-c showed that the product obtained by this method contained no cyclobutanol or allylcarbinol.

Cyclobutanol. In one preparation of cyclopropylcarbinol an unforeseen secondary reaction occurred during the hydrolysis step. Material dispersed accidentally was collected and mixed with 10% sulfuric acid. The acidic solution was allowed to stand for nine days before it was continuously extracted with ether for two days. Distillation afforded 5.0 g., b.p. 102-116°, n_D^{25} 1.4312 (I) and 13.2 g., b.p. 116-118°, n_D^{25} 1.4327 (II). The infrared spectrum of fraction II was superimposable with that of cyclobutanol as obtained by Silver (138) and by Mazur (109) by the reduction of cyclobutanone. Roberts and Sauer (39) report for cyclobutanol b.p. 125°, n_D^{25} 1.4347 and Silver (138) reports b.p. 119-120°, n_D^{25} 1.4333-1.4340. Analysis by v-p-c of the material obtained in the present reaction showed it to be about 95% cyclobutanol containing a small amount of allylcarbinol and no cyclopropylcarbinol. The total yield of cyclobutanol obtained was 18.6% based on the cyclopropanecarboxylic acid originally used in the experiment.

Cyclopropylcarbinol and Phosphorous Tribromide. The reaction was run according to the procedure of Roberts and Mazur (38). In a typical run, 43.2 g. (0.60 mole) of cyclopropylcarbinol and 72 g. (0.266 mole) of phosphorous tribromide afforded 69.5 g. (85.9%) of mixed bromides, b.p. 103-109°. The fractions were analyzed by v-p-c and by analogy with the chromatograms for the isomeric alcohols and

chlorides, the peaks in the chromatograms on column A at 70° were assigned, in order of increasing retention time, to allylcarbinyl, cyclobutyl and cyclopropylcarbinyl bromides. The relative amounts of each component were determined by weighing the areas from the chromatogram and varied only slightly from run to run. In the particular run described, the product consisted of 5.7% allylcarbinyl bromide, 20.1% cyclobutyl bromide and 74.2% cyclopropylcarbinyl bromide. The infrared spectrum of the mixture was identical to that obtained by Roberts and Mazur (38) who obtained a 70% overall yield of bromides, b.p. 102-112°. The n-m-r spectrum of the mixture was, as expected, extremely complex. The doublet observed for the methylene group in the cyclopropylcarbinyl bromide and the complex pattern usually observed for the cyclopropyl ring protons were clearly evident, however, and substantiate the conclusion that the predominant isomer in the mixture was cyclopropylcarbinyl bromide.

Cyclopropylacetonitrile (Cyclopropylcarbinyl Cyanide). The procedure was suggested by the sketchy report given by Von Braun and his co-workers (77). Many runs were made in an attempt to find optimum conditions for this reaction. The following procedure represents the best conditions found in this study. Sodium cyanide (11.0 g., 0.224 mole) was dissolved in 110 ml. of 80% ethanol by heating the mixture for a few minutes on a steam bath. To this solution was added 25.2 g. (0.187 mole) of the cyclopropylcarbinyl bromide mixture obtained above and the homogeneous mixture was heated at reflux for 1.5 hr. The dark mixture was cooled, diluted with water and extracted

several times with chloroform. The combined dark chloroform extracts were dried over sodium sulfate. The chloroform was removed by distillation on a steam bath and the residue was distilled through a 30-cm. wire-spiral packed column. The product was collected at 138-143° (8.0 g.) with the main fraction (7.2 g.) at 140-143° (Von Braun and co-workers reported (77) b.p. 142-144°). Analysis by v-p-c indicated that the fractions collected at 110-130° consisted of a large number of components including recovered cyclobutyl bromide. The fractions, b.p. 138-143°, consisted of three components (A, B and C) in relative percentages of 76.4: 22.6: 1.0, as determined by weighing the areas in the vapor-phase chromatograms. Infrared and n-m-r evidence strongly indicated that the main two components (A and B) were cyclopropylacetonitrile(A) and allylcarbinyl cyanide(B). The infrared spectrum of the mixture had a strong nitrile band at 2250 cm^{-1} and a very weak olefin band at 1650 cm^{-1} . There were also strong cyclopropyl bands at 1025 cm^{-1} and 3080 cm^{-1} . The n-m-r spectrum had weak resonances in the vinyl-proton region and, at higher field, a strong doublet followed by a complex multiplet typical of the methylene ring-protons of a monosubstituted cyclopropane. The yield of the mixture is 52.8% based on the total amount of bromides taken and 66.0% based on the total of cyclopropylcarbinyl and allylcarbinyl bromides present in the starting material. Attempted separation of the isomeric nitriles by distillation through a center-rod column was unsuccessful. A sample rich in component B was obtained from the mixture by v-p-c using a preparative column and

consisted of about 80% B. Its infrared spectrum exhibited a nitrile band at 2250 cm^{-1} , another band at 2200 cm^{-1} (?) and bands at 1650 cm^{-1} , 995 cm^{-1} and 920 cm^{-1} , characteristic of a terminal vinyl group. These bands are absent in a fraction obtained by preparative v-p-c in which component B was absent. The evidence seems compelling that B is the open-chain isomer, allylcarbinyl cyanide. No evidence has been obtained as to the identity of C, the minor impurity in the product mixture.

In a run starting with 126.3 g. of the isomeric bromides, the yield of nitriles of b.p. $142-146^\circ$ was 47.7 g. (60.6% and 75.9%, determined as above).

Purification of Cyclopropylacetonitrile. The mixture of nitriles obtained above was treated with potassium permanganate as described in the purification of 1-methylcyclopropanecarbonitrile (see page). The resulting mixture was continuously extracted with pentane or with ether. The extracts were dried over potassium carbonate and distilled. In one run, 19.1 g. of the crude mixture afforded 8.1 g. of cyclopropylacetonitrile, b.p. $140-145^\circ$, n_D^{25} 1.4220, which showed only one peak in its vapor-phase chromatogram. In another run, 47.7 g. of the mixture afforded 36.7 g., b.p. $145-146^\circ$, n_D^{25} 1.4224. The n-m-r spectrum of the purified material had no peaks in the vinyl-proton region and showed a doublet for the methylene protons, split by the adjacent tertiary proton on the ring, and a highly split pattern characteristic of the tertiary ring proton and the other ring protons. Despite the

simplicity of the vapor-phase chromatograms, a satisfactory elemental analysis could not be obtained on samples from either of these preparations.

Anal. Calcd. for C_5H_7N : C, 74.03; H, 8.70; N, 17.27. Found: C, 72.43; H, 8.82; N, 17.17.

Cyclopropylacetaldehyde. Reduction of Cyclopropylacetonitrile

(Attempted). The procedure was similar to that which proved successful in the reduction of cyclopropanecarbonitrile and other nitriles (see above). Three unsuccessful runs were made using the mixture of cyclopropylacetonitrile and allylcarbinyl cyanide reported above. A typical run will be described. To 3.0 g. (0.037 mole) of the nitrile mixture in 12 ml. of dry ether, stirred and cooled in a Dry-Ice-acetone bath, was added dropwise 16 ml. (0.0102 mole) of 0.65 N lithium aluminum hydride solution, prepared and titrated as described earlier. The mixture was stirred for 1 hr. at -80° and was then allowed to gradually warm up to 5° over the course of 5 hr. The mixture was hydrolyzed with 2 N sulfuric acid, the layers were separated and the acid solution was extracted several times with ether. The ethereal solution was dried over sodium sulfate. After the ether had been carefully removed by distillation through a 30-cm. column packed with glass helices, the residue (amounting to only 1 g.) was distilled through a 30-cm. wire-spiral packed column. There was collected 0.5 g. of a mixture of several components, according to v-p-c, and 0.5 g. of a tarry residue remained. The distillate gave a positive test with 2,4-dinitrophenylhydrazine reagent and showed characteristic aldehyde absorption bands

in its infrared spectrum. The spectrum also indicated the presence of olefinic compounds. The acidic solution from hydrolysis of the original reaction mixture was made basic and extracted with ether. From these extracts, distilled in vacuo, there was obtained 0.5 g. of material that smelled strongly of amine and had an infrared spectrum indicative of an unsaturated amine. There was left 0.9 g. of tarry material. The complexity of the reaction products and the poor yield obtained discouraged further work on this method of synthesis of cyclopropylacetaldehyde.

Allylcyclopropane. Cyclopropylmagnesium chloride was prepared from cyclopropyl chloride by the procedure of Ramsden et al. (140). In a typical run, 23.0 g. (0.30 mole) of cyclopropyl chloride(41), 8.5 g. (0.35 mole) of magnesium and 65 g. (0.90 mole) of purified tetrahydrofuran were used. Tetrahydrofuran was purified by being heated at reflux over potassium hydroxide pellets and was distilled from lithium aluminum hydride; b.p. 65°. A portion of the chloride solution in tetrahydrofuran was added to the magnesium in a nitrogen atmosphere, the stirrer was started and 1 ml. of ethylene dibromide was added to initiate formation of the Grignard reagent. The mixture became warm and darkened almost immediately. The balance of the chloride solution was added dropwise at such a rate as to maintain reflux. The mixture was stirred for 24 hr. at reflux in a nitrogen atmosphere and was then filtered through a plug of glass wool to remove unreacted magnesium (3 g.). To the dark Grignard solution was slowly added dropwise 26.6 g. (0.22 mole) of allyl bromide. The mixture warmed to reflux spontaneously and

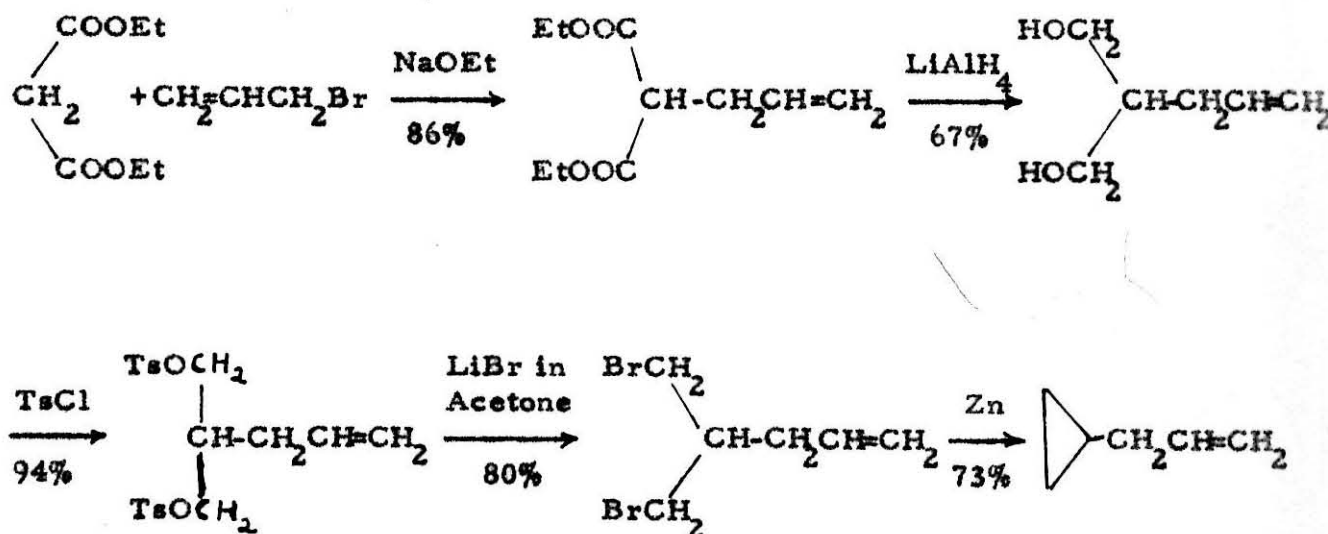
occasionally had to be cooled in an ice bath due to the vigorous reaction which took place. The mixture was stirred at reflux for 24 hr. and was then poured over crushed ice. The yellow-orange organic layer was separated and washed twice with water before being dried over potassium carbonate. Distillation afforded 15.0 g. of material which had b.p. 55-64°, n_D^{25} 1.4088-1.4113. Analysis by v-p-c gave the product composition as 55% allylcyclopropane, 40% tetrahydrofuran and 5% of another component which is probably diallyl.* The retention time of the main component was identical with that of an authentic sample of allylcyclopropane prepared by White (79) (see below). Based on this composition, the yield of allylcyclopropane was about 8 g. (45%). The infrared spectrum of a fraction, b.p. 56-59°, from a previous preparation was identical with that of White's pure allylcyclopropane (79). Further purification of allylcyclopropane as prepared above was not carried out or deemed necessary for the next step in the synthetic scheme.

Attempts were made to prepare allylcyclopropane by a coupling reaction between allyl bromide and cyclopropyllithium, prepared by the method of Hart and Sandri (141). The procedure was basically that

*This composition, based on the peak areas in the vapor-phase chromatogram, can only be considered approximate since, with compounds of as diverse functionality as allylcyclopropane and tetrahydrofuran, the ratio of the areas in the chromatogram may not be at all directly proportional to the composition of the mixture by weight.

as described above for cyclopropylmagnesium chloride. The product consisted mainly of recovered allyl bromide containing some allylcyclopropane and biallyl. The total yield was much less than was obtained in the Grignard reaction.

Some of the allylcyclopropane used in the syntheses to be described below was prepared by White (79) by an alternate method outlined below. White obtained pure allylcyclopropane, according to v-p-c, which had b. p. 65-66°, n_D^{25} 1.4084.



3-Cyclopropyl-1,2-propanediol. The procedure was based on procedures of Swern and co-workers (142) and Roberts and Sauer (139) for the hydroxylation of olefins with performic acid. In some runs, allylcyclopropane which had been prepared by White (see above) was used while in other runs allylcyclopropane as prepared by the Grignard

reaction (see above) was used. The yields of product were comparable from the two sources of starting material. A typical preparation is described. In a 300-ml. three-necked flask, fitted with a thermometer, mechanical stirrer and dropping funnel, were mixed 130 ml. of 90% formic acid and 18.6 g. (0.165 mole) of 30% hydrogen peroxide. To this mixture was slowly added 12.3 g. (0.15 mole) of allylcyclopropane at such a rate that the temperature of the reaction mixture did not exceed 32°. An ice bath had to be applied intermittently to moderate the reaction. The addition required 30 min. The mixture became homogeneous after 2 hr. of stirring. Stirring was continued overnight, and the formic acid was then removed in vacuo (water aspirator) on a steam bath. The residue was cooled and treated with an ice-cold solution of 12 g. of sodium hydroxide in 25 ml. of water in small portions. The mixture became warm when stirred and had to be cooled in an ice bath. The aqueous solution was continuously extracted with ether (ethyl acetate was used in one run) for 24-48 hr. and the extracts were dried over sodium sulfate. After distillation of the solvent, the residue was distilled in vacuo to give 14.8 g. (85.3%) of 3-cyclopropyl-1,2-propanediol, b.p. 87-88° (1.5 mm.), n_D^{25} 1.4636, as a colorless viscous liquid. The structure was assumed on the basis of the synthetic method and the presence in the infrared spectrum of a broad hydroxyl band at 3400 cm^{-1} and cyclopropyl bands at 1020 cm^{-1} and 3080 cm^{-1} and the absence of bands due to carbonyl groups and olefinic unsaturation.

Cyclopropylacetaldehyde. II. Cleavage of 3-Cyclopropyl-1,2-

propanediol. Several runs were carried out. Xylene, which was used as solvent in preliminary experiments, was found to be inferior to methylene chloride which was used in all later experiments. A typical run will be described in detail. 3-Cyclopropyl-1,2-propanediol (10.7 g., 0.092 mole) was dissolved in 40 ml. of methylene chloride in a 200 ml. three-necked flask equipped with a mechanical stirrer, reflux condenser and dropping funnel. A solution of 60 g. (0.135 mole) of lead tetraacetate in 150 ml. of methylene chloride was added rapidly in portions from the dropping funnel, as the mixture warmed spontaneously to reflux.* Shortly after all the reagent had been added, a white precipitate suddenly separated. The mixture was stirred at room temperature for 3 hr. and was then filtered to remove the precipitated lead acetate (26 g., 87%). The filtrate was extracted with five 50-ml. portions of 15% sodium carbonate solution. In the initial extractions, there was much frothing as a fine brown precipitate of lead dioxide formed which remained in the aqueous phase and was separated with that phase in the separatory funnel. Extraction was continued until the frothing and formation of lead dioxide ceased. The methylene chloride solution was dried over sodium sulfate. The solvent was distilled through a 30-cm. column packed with glass helices and the residue was distilled through a 30-cm. wire-wpiral packed column. The following fractions were obtained and analyzed by v-p-c.

*It is important to use fresh white lead tetraacetate in this reaction in order to obtain maximum yields.

Fraction	Temp., °C	Wt., g.	% $\triangle\text{CH}_2\text{CHO}$ by <u>v-p-c</u>	n_D^{25}
I	92-102	0.24	40	-
II	102-104	1.00	70	-
III	104-106	0.66	80	-
IV	106-107	3.56	95	1.4196
Residue		1.3		

The main impurity in Fractions II-IV was a component with slightly shorter retention time by v-p-c than for cyclopropylacetaldehyde, and may be some penten-4-al due to the diallyl contaminant in the allyl-cyclopropane used originally in the synthetic scheme. The total yield of cyclopropylacetaldehyde, taken as II-IV, was 5.22 g. (67.5%). In runs in which 3-cyclopropyl-1,2-propanediol was derived from pure allylcyclopropane which had been prepared by White (see above), the yield of cyclopropylacetaldehyde of 98-99% purity, as determined by v-p-c, was 68.2% and 57.5% in two runs. The product had b.p. 104-106°, n_D^{25} 1.4180-1.4207, and had an infrared spectrum identical to that of Fraction III above and was also identical to that of cyclopropylacetaldehyde as prepared by the reduction of N,N-dimethylcyclopropylacetamide (see page 113). A spectrum of aldehyde in a 1.0 mm. micro cell showed bands at 1.65 μ and 2.20 μ which are said to be diagnostic for the presence of a cyclopropane ring (143). The n-m-r spectrum supports the structural assignment; the low-field resonance of the aldehyde proton appears as a triplet; a doublet at higher field, each peak

of which is further split into two, is ascribed to the α -methylene group, and the complex resonance at still higher field is due to the ring protons. The spectral data, taken with the method of synthesis, established the product as cyclopropylacetaldehyde.

A sample of cyclopropylacetaldehyde was purified by v-p-c on preparative Column "A". A sample was obtained, n_D^{25} 1.4205, which was at least 99% pure, according to v-p-c. However, a satisfactory analysis was not obtained for this material.

Anal. Calcd. for C_5H_8O : C, 71.39; H, 9.59. Found: C, 69.55; H, 9.80.

The disagreement between the analytical results and the v-p-c analysis suggests that the sample was contaminated by non-volatile peroxy compounds, formed on contact with air, which did not appear in the chromatogram. An analytically pure sample of cyclopropylacetaldehyde was prepared by redistillation under nitrogen through a 30-cm. wire-spiral packed column, as described for 1-methylcyclopropanecarboxaldehyde (see page 93). The sample submitted for elemental analysis had b. p. 102.5-103.5° (744 mm.), n_D^{25} 1.4182.

Anal. Calcd. for C_5H_8O : C, 71.39; H, 9.59. Found: C, 71.36; H, 9.49.

Cyclopropylacetaldehyde was prepared by Hart and Wyman (40) by the catalytic dehydrogenation of 2-cyclopropylethanol over a copper-silver catalyst. The aldehyde prepared in this way had b. p. 105-106°, n_D^{25} 1.4238 (see footnote, page 116). No elemental analysis of a sample

of the aldehyde was reported by these workers. In unpublished work, Urry and Hartzler (63) prepared cyclopropylacetaldehyde by oxidation of 2-cyclopropylethanol with chromic acid-pyridine. They obtained an aldehyde, b.p. 69-75° (160 mm.), n_D^{20} 1.3891, and recovered alcohol. Their aldehyde was probably impure, as indicated by the low index of refraction and unsatisfactory elemental analysis data.

Cyclopropylacetaldehyde 2,4-dinitrophenylhydrazone, recrystallized from ethanol, had m.p. 137.0-138.5°. The same derivative, described on page 114, had m.p. 141.5-143.0° and gave a correct elemental analysis; mixed m.p. of the two samples was undepressed at 139.3-140.7°. Urry and Hartzler (63) prepared the same derivative which had m.p. 118-119° and for which a satisfactory analysis for nitrogen was obtained.

Cyclopropylacetaldehyde p-nitrophenylhydrazone was prepared and recrystallized twice from ethanol-water to give yellow-orange needles, m.p. 116.6-117.8°. A sample gave a correct elemental analysis. Hart and Wyman (40) report m.p. 110-110.5° for the same derivative. A sample of the material prepared by Hart and Wyman (kindly supplied by Prof. Hart) was found to have m.p. 112-115°; mixed m.p. with the above sample was undepressed at 114-115°.

Anal. Calcd. for $C_{11}H_{13}N_3O_2$: C, 60.26; H, 5.98. Found: C, 60.37; H, 6.08.

Cyclopropylacetaldehyde semicarbazone was prepared earlier (see page 115) and had m.p. 140.8-142.2°. A sample gave a satisfactory elemental analysis.

Cyclobutanecarboxylic acid was prepared by the acid hydrolysis of 600 g. (3.0 moles) of 1,1-dicarbethoxycyclobutane (144) according to the method of Cason and Allen (145). There was obtained 173.9 g. (58%) of cyclobutanecarboxylic acid, b.p. 104.0-106.5° (22.5 mm.), n_D^{25} 1.4427 (lit. (145, 96) b.p. 104-106° (21 mm.); b.p. 93° (16 mm.), n_D^{25} 1.4413). The $n-m-r$ spectrum of this material showed a resonance at very low field due to the acid proton and a complex symmetrical multiplet at high field for the resonances of the ring protons.

Cyclobutylcarbinol was prepared by the reduction of 100 g. (1.0 mole) of cyclobutanecarboxylic acid with 46.8 g. (1.23 mole) of fresh lithium aluminum hydride in 500 ml. of dry ether by standard procedures. Hydrolysis and distillation afforded 72.3 g. (84.2%) of cyclobutylcarbinol, b.p. 140.5-141.5°, n_D^{25} 1.4445 (lit. (146), b.p. 140-141°, n_D^{25} 1.4430). The $n-m-r$ spectrum showed a hydroxyl-proton resonance, a doublet for the protons on the methylene group and a generally symmetrical pattern for the ring-protons, similar to that found in the spectrum of cyclobutanecarboxylic acid.

Cyclobutanecarboxaldehyde. I. Oxidation of Cyclobutylcarbinol.

The method was adapted from that used by Kuhn and Grundmann (147) and by Weygand (148) for the preparation of low-molecular weight

aldehydes. A 200-ml. three-necked flask was equipped with a dropping funnel and a condenser arranged for downward steam distillation. In the later stages, a steam inlet was also connected to the flask. In the flask was placed 15 g. (0.175 mole) of cyclobutylcarbinol which was heated to its boiling point. To the hot alcohol was added a solution of 17.5 g. (0.058 mole) of sodium dichromate and 15 g. of sulfuric acid in 50 ml. of water over a 15 min. period. The solution turned very dark almost immediately as the volatile materials distilled from the flask with steam. A slow stream of steam was passed through the system for 30 min. The ice-cooled distillate consisted of two phases which were separated. The organic layer was dried over calcium chloride and then distilled through a 30-cm. wire-spiral packed column to give 1.8 g. of a two-phase mixture, b.p. 70-104°, in several fractions. An additional 0.67 g. was obtained by continuous extraction of the aqueous layer of the steam distillate with ether, then desiccation with magnesium sulfate and distillation. There was also obtained 7.4 g. of a higher-boiling fraction which was indicated by v-p-c to consist of aldehyde, recovered cyclobutylcarbinol and several other components. The infrared spectrum of this material was characteristic of an aldehyde, with a carbonyl band at 1725 cm^{-1} and aldehyde C-H bands at 2700 and 2800 cm^{-1} . Extraneous peaks in the spectrum suggested that there were impurities in the aldehyde. The product was probably mainly cyclobutanecarboxaldehyde.

The 2,4-dinitrophenylhydrazone was prepared and recrystallized from ethanol, m.p. 153.8-155.1°. Slobodin and Blinova (81) report m.p. 153-154° for cyclobutanecarboxaldehyde 2,4-dinitrophenylhydrazone, while Brown and Subba Rao (69) report m.p. 155-156°.

Anal. Calcd. for $C_{11}H_{12}N_4O_4$: C, 50.50; H, 4.58. Found: C, 50.27; H, 4.67.

Cyclobutanecarbonyl Chloride was prepared from 40 g. (0.40 mole) of cyclobutanecarboxylic acid and 60 g. (0.50 mole) of thionyl chloride by standard procedures. The yield of product, b.p. 129-136° (mostly 135-136°), was 41.8 g. (88.5%).

N-Methylcyclobutanecarboxanilide. Cyclobutanecarbonyl chloride (41.8 g., 0.35 mole) was dissolved in 100 ml. of benzene and to the solution was added a solution of 85 g. (0.80 mole) of N-methylaniline in 100 ml. of benzene over a 30 min. period. The mixture became very warm shortly after addition was commenced and a solid formed which made stirring difficult. The mixture was cooled in an ice bath during the balance of the addition. The mixture was then heated for 1 hr. at reflux. Cooled 3 N hydrochloric acid (150 ml.) was added and the layers were separated. The benzene layer was extracted with 50 ml. of 3 N hydrochloric acid and 50 ml. of 15% sodium carbonate solution. Removal of benzene on a steam bath left a reddish residue of N-methylcyclobutanecarboxanilide amounting to 60.5 g. (91%). The oily residue solidified when cooled and scratched, but the solid could not be recrystallized from common solvents as it invariably came out of solutions as an oil. The infrared spectrum of the product was consistent with the

structural assignment. There was a band at 1660 cm^{-1} characteristic of tertiary amides and the usual bands associated with an aromatic group. There are no extraneous bands in the spectrum.

A sample of N-methylcyclobutanecarboxanilide, b.p. $108-125^\circ$ (1 mm.), was recovered after treatment with lithium aluminum hydride (see below) as a yellow-orange liquid. This sample was recrystallized by being repeated dissolution in pentane and crystallization in a Dry Ice-acetone bath. The various operations had to be carried out in a cold room because of the low melting point of the solid. White crystals were obtained, m.p. $25.0-27.0^\circ$, which were submitted for analysis which, however, was not satisfactory.

Anal. Calcd. for $\text{C}_{12}\text{H}_{15}\text{NO}$: C, 76.15; H, 7.99. Found: C, 74.83; H, 7.92.

Cyclobutanecarboxaldehyde. II. Reduction of N-Methylcyclobutanecarboxanilide. Several trials of this reaction were made following the general procedure given by Weygand and co-workers (80). A typical run will be described. The yields varied only slightly as the proportions of starting materials were varied over a limited range. To 17.8 g. (0.094 mole) of N-methylcyclobutanecarboxanilide in 100 ml. of purified tetrahydrofuran (see page 123), cooled in an ice-salt bath below 0° and stirred mechanically, was slowly added a suspension of 1.4 g. (0.037 mole) of lithium aluminum hydride in 50 ml. of tetrahydrofuran. The mixture was stirred for 2 hr. in the cooling bath.

To the mixture was carefully added enough 2 N sulfuric acid to make the mixture acidic. There was some frothing during the initial stages of the hydrolysis. The layers were separated and the aqueous layer was extracted with ether. The organic extracts, which gave a strong test with 2,4-dinitrophenylhydrazine reagent, were dried over sodium sulfate. Most of the solvents were removed by distillation through an 80-cm. column packed with glass helices (it was necessary to use a large distilling flask during this distillation because of considerable frothing). The residue was distilled through a spinning-band column (a 30-cm. wire-spiral packed column was used in later runs with equal effect). The fractions collected were as follows.

Fraction	Temp., °C	Wt., g.	Composition according to v-p-c		
			% \square CHO	% \square CH ₂ OH	% Solvents
I	50-90	0.20	10	-	90
II	90-97	0.11	60	-	40
III	97-102	0.08	85	-	15
IV	102-107	0.14	96	-	4
V	107-109	1.59	99.5	0.3	0.2
VI	109-120	0.40	99.9	-	0.1
VII	120-138	0.41	10	80	10
VIII	30-108(1 mm.)	0.23			
IX	108-125(1 mm.)	2.58			
Residue		3.3			

A white crystalline solid separated from Fraction VI after distillation. The v-p-c analysis given in the distillation table is of the residual liquid phase.

The infrared spectrum of Fraction V was substantially the same as that of cyclobutanecarboxaldehyde as obtained by the oxidation of cyclobutylcarbinol (see page 131) except that the present spectrum did not contain the peaks in the earlier spectrum which were ascribed to impurities. The n-m-r spectrum of Fraction V showed a doublet at very low field strength for the aldehyde-proton resonance and a complex multiplet at high field typical of cyclobutane ring-proton resonances. The yield of cyclobutanecarboxaldehyde, Fractions III-V, was 1.81 g., which was 22.8% of theory based on the original amount of starting material and 26.7% based on non-recovered N-methylcyclobutanecarboxanilide. A sample of Fraction V was submitted for analysis, but a satisfactory analysis was not obtained. Purification by preparative v-p-c did not improve the analytical results.

Anal. Calcd. for C_5H_8O : C, 71.39; H, 9.59. Found:
C, 68.59; H, 9.67.

An analytically pure sample was prepared by distillation in a nitrogen atmosphere after the aldehyde had been dried over Drierite (for details see page 93) and had b.p. 102.5-103.0°, n_D^{25} 1.4286. As in the cases of the other aldehydes discussed earlier, impure cyclobutanecarboxaldehyde probably contained peroxygenated impurities.

Anal. Calcd. for C_5H_8O : C, 71.39; H, 9.59. Found:
C, 71.28, 71.28; H, 9.47, 9.60.

Slobodin and Blinova (81) reported the preparation of cyclobutanecarboxaldehyde, b.p. 113-115°, n_D^{20} 1.4357, by passage of

cyclobutanecarboxylic acid and formic acid through a hot tube. No analytical data for the aldehyde was reported.

The higher-boiling component in Fractions V-VII was identified as cyclobutylcarbinol by comparison of infrared spectra and retention times by v-p-c with that of authentic material (see above). Fraction VIII also consisted mainly of cyclobutylcarbinol along with smaller amounts of other components. The yield of cyclobutylcarbinol was 9.3% on the basis of non-recovered N-methylcyclobutanecarboxanilide. Fraction IX was recovered starting material, according to its infrared spectrum. The residue also contained considerable starting material, according to its infrared spectrum, but other unidentified components were also present.

The white crystals which settled out of Fraction VI (and similar fractions in other runs) were recrystallized from methanol to give white needles, m.p. 118.2-120.5°. The infrared spectrum of this substance indicated the complete absence of carbonyl and hydroxyl bands, but there was considerable absorption in the region 1000-1200 cm^{-1} , characteristic of ether linkages. The n-m-r spectrum showed a doublet at low field and a series of resonances at high field characteristic of a mono-substituted cyclobutane. This evidence, together with analytical data, indicates that the solid is a polymer of cyclobutanecarboxaldehyde, and was perhaps the cyclic trimer.

Anal. Calcd. for $(\text{C}_5\text{H}_8\text{O})_n$: C, 71.39; H, 9.59. Found: C, 71.57; H, 9.69.

Dimethylcyclopropylacetonitrile. The alkylation of cyclopropylacetonitrile was carried out by the general method described recently by Newman and co-workers (82). The following procedure represents the best of several investigated. A suspension of sodamide in 500 ml. of liquid ammonia was prepared from 17.5 g. (0.76 g. atom) of sodium. To this suspension, cooled in a Dry Ice-acetone bath, was rapidly added from a dropping funnel 6 g. of purified cyclopropylacetonitrile. Methyl bromide was then added as follows. A weighed amount of methyl bromide (125 g., 1.31 moles) was condensed in a Dry Ice-cooled round-bottomed flask. The flask was attached by means of a stopcock and Tygon tubing to the top of a Dry Ice-condenser attached to the three-necked reaction flask. Methyl bromide was allowed to warm and vaporize slowly into the condenser in which it condensed and dripped into the reaction flask. In this way a steady slow rate of addition of methyl bromide was maintained. In other runs, the methyl bromide was added through a Dry Ice-cooled dropping funnel and the rate of addition could not be controlled easily. Occasional violent eruptions, resulting in loss of material, occurred whenever too much methyl bromide was added at one time. By the preferred procedure, after about 30 g. of methyl bromide had been added, the addition was stopped and another 9.7 g. (total 15.7 g., 0.195 mole) of cyclopropylacetonitrile was added rapidly. The rest of the methyl bromide was added as before over an additional period of 2 hr. The cooling bath was then removed and the mixture was stirred at reflux for 8.5 hr. The ammonia was

allowed to evaporate and ethyl ether was added to the system. Enough water was then added to dissolve the inorganic salts. The aqueous solution was then continuously extracted with ether overnight. The ether was distilled through a 30-cm. Vigreux column on the steam bath and the residue was then distilled through a small distillation head with Vigreux indentations in the side arm. There was collected 13.9 g. (65.7%) of dimethylcyclopropylacetonitrile, b.p. 140-145°. The v-p-c analysis indicated only one component in all the fractions to the extent of 95% and to at least 99.5% in later fractions. Apparently no cyclopropylacetonitrile was recovered. A sample of the best fractions was redistilled through a 30-cm. wire-spiral packed column, and had b.p. 141.0-143.5°, n_D^{25} 1.4173.

Anal. Calcd. for $C_7H_{11}N$: C, 77.01; H, 10.16; N, 12.83. Found: C, 76.88; H, 10.18; N, 12.75.

The infrared spectrum of dimethylcyclopropylacetonitrile has a nitrile band at 2250 cm^{-1} and cyclopropyl bands at 1025 cm^{-1} and 3090 cm^{-1} . The n-m-r spectrum showed that the product was exclusively the dimethylated nitrile. There was a large unsplit resonance for the six methyl protons and a complex pattern at slightly higher fields characteristic of a mono-substituted cyclopropane. There were no resonances or splittings as expected for protons in a methylene or methyne group on the side chain.

Dimethylcyclopropylacetaldehyde was prepared by the reduction of dimethylcyclopropylacetonitrile with lithium aluminum hydride by

the general method described earlier. To 13.0 g. (0.119 mole) of dimethylcyclopropylacetonitrile in 100 ml. of ether cooled in a Dry Ice-acetone bath at -50° was added 80 ml. (0.037 mole) of 0.46 M lithium aluminum hydride in ether. A milky white suspension formed immediately. The mixture was stirred for 8.5 hr. as the bath temperature was allowed to rise slowly to 0° . The mixture was hydrolyzed with 10% sulfuric acid until the solution was acidic. The acidic solution was continuously extracted with ether for 36 hr. and the ethereal extracts were dried over magnesium sulfate. Ether was distilled through a 30-cm. column packed with glass helices and the residue was distilled through a 30-cm. wire-spiral packed column. There was collected 10.7 g. of material, b.p. $115-133^{\circ}$. According to v-p-c analyses, all of the fractions consisted of at least 90% dimethylcyclopropylacetaldehyde (identified below) while the best fractions, b.p. $129-133^{\circ}$ (744 mm.), n_D^{25} 1.4250, consisted of at least 98% aldehyde. Redistillation in a nitrogen atmosphere as before (see page 93) afforded an analytically pure sample, n_D^{25} 1.4250.

Anal. Calc. for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 74.93, 74.82; H, 10.75, 10.82.

The aldehyde was identified by its n-m-r spectrum. The spectrum was very similar to that described above for dimethylcyclopropylacetonitrile except that the resonance for the six methyl protons occurred at higher field in the case of the aldehyde.

In some preliminary experiments in which the lithium aluminum hydride solution was not titrated before use, the product consisted of mixtures of nitrile and aldehyde, which could not be separated readily by distillation.

The 2,4-dinitrophenylhydrazone was prepared and recrystallized from ethanol-water. After being dried in vacuo, the orange platelets exhibited unusual behavior on melting. This behavior was reproducible on recrystallization or on remelting of the solidified melt. A portion of the solid melted at 126.5-127.0° and the system remained unchanged until the rest of the solid melted sharply at 132.5-133.0°.

Anal. Calcd. for $C_{13}H_{16}N_4O_4$: C, 53.42; H, 5.52; N, 19.17.

Found: C, 53.34; H, 5.60; N, 19.14.

Ethyl cyclopropanecarboxylate was prepared from cyclopropanecarboxylic acid, ethyl alcohol and sulfuric acid by heating the mixture at reflux for 24 hr. The product had b.p. 74-77° (110 mm.), n_D^{25} 1.4154 (lit. (111) b.p. 133.0-133.5°).

Dimethylcyclopropylcarbinol was prepared in 70% yield by the reaction of ethyl cyclopropanecarboxylate and methylmagnesium chloride in ether, and had b.p. 120-121° (743.5 mm.), n_D^{25} 1.4307 (lit. (83 , 138) b.p. 123.7° (760 mm.), n_D^{20} 1.4335; b.p. 121-123°, n_D^{25} 1.4338). Much lower yields of product were obtained when methylmagnesium iodide was used in place of the chloride.

Isopropenylcyclopropane was prepared by the method of Slabey and Wise (83). Dimethylcyclopropylcarbinol and 1 drop of sulfuric acid were heated at reflux in an oil bath at 140-170° as the products distilled

out of the reaction mixture through a short Vigreux column. The two-phase distillate, b.p. 55-95°, was composed of water, isopropenylcyclopropane and recovered alcohol. The layers were separated and the organic layer was dried over Drierite. Isopropenylcyclopropane was separated by distillation through a 30-cm. spiral-wire packed column and had b.p. 69.0-69.5° (745.0 mm.), n_D^{25} 1.4227 (lit. (83) b.p. 70.3° (760 mm.), n_D^{20} 1.4255). The yield of olefin based on non-recovered alcohol was 66%. The $n-m-r$ spectra of the olefin has an unsplit low-field resonance for the vinyl protons, a singlet for the methyl protons followed at higher field by multiplets characteristic of the tertiary and methylene protons of a cyclopropane ring, in agreement with the assigned structure. The infrared spectrum of the product has bands characteristic of cyclopropane compounds at 1020 cm^{-1} and 3090 cm^{-1} and bands characteristic of 1,1-disubstituted ethylenes at 890 cm^{-1} and 1640 cm^{-1} .

Isopropylcyclopropane was prepared by hydrogenation of isopropenylcyclopropane over platinum black in ethanol at room temperature and atmospheric pressure. In two runs, 1.05 and 1.01 moles of hydrogen were taken up per mole of olefin before the rate of hydrogen uptake became imperceptible. The mixture was filtered to remove the platinum and the filtrate was diluted with water. The hydrocarbon was separated, washed with water and dried over calcium chloride. The dried product had n_D^{25} 1.3800 and had one unsymmetrical peak in its vapor-phase chromatogram (Column "A", 40°). Kazanskii and

co-workers (149) report that 1 mole of isopropenylcyclopropane took up 1.3 moles of hydrogen under these conditions to give a mixture of 70% isopropylcyclopropane and 30% 2-methylpentane. Comparison of the index of refraction of the product obtained in this work (n_D^{25} 1.3800) with that of pure isopropylcyclopropane (n_D^{20} 1.3865) (150) and pure 2-methylpentane (n_D^{25} 1.3689) (151) indicates that our product is a mixture of approximately 75% isopropylcyclopropane and 25% 2-methylpentane. There was no recovered olefin in the product mixture. The infrared spectrum of the product was compared with that of 2-methylpentane. All the peaks found in the spectrum of 2-methylpentane are in the spectrum of the hydrogenation product, but in addition there are several minor peaks and two strong bands at 1020 cm^{-1} and 3100 cm^{-1} , characteristic of cyclopropane compounds. The n - m - r spectra of the mixture and of 2-methylpentane were also compared. The spectrum of the mixture is complex since the chemical shifts between the various types of protons in the molecules apparently are small. The expected doublet for the methyl protons in isopropylcyclopropane is obscured by other resonances. The most salient difference between the spectra of the hydrogenation mixture and pure 2-methylpentane is the appearance in the former spectrum of two resonances at high field, each a partially resolved multiplet. Such high-field resonances are characteristic of protons on cyclopropane rings. The evidence therefore indicates that the hydrogenation product is a mixture of isopropylcyclopropane and 2-methylpentane in a ratio of about 3:1.

Decarbonylation Experiments, General Procedure. The procedure used in the decarbonylation of low-boiling aldehydes was as follows. An approximately 10% solution of the aldehyde in diphenyl ether (redistilled, b.p. 84.5-87.0° (1 mm.), n_D^{25} 1.5787) was prepared in a small three-necked flask equipped with a magnetic stirrer, a dropping funnel, a reflux condenser and a nitrogen inlet. The condenser was connected in series with an air-cooled cold finger, a small Dry Ice-cooled trap with a removable top, another small air-cooled cold finger, and an inverted graduated cylinder or graduated separatory funnel in which the non-condensable gases were collected by displacement of water. The entire system was flushed with nitrogen for 5-10 min. and the reaction flask was then immersed in a magnetically stirred oil bath, maintained at the desired temperature by a Cenco-De Khotinsky Thermo-Regulator. After 1-2 min., the nitrogen flow was stopped and the inlet was quickly stoppered. The contents of the flask were allowed to come to the reaction temperature over about 10 min. When displacement of nitrogen, due to changes in pressure on warming the system, had ceased, the first portion of di-t-butyl peroxide (redistilled, b.p. 57-58° (120 mm.), n_D^{25} 1.3866) was added through the dropping funnel. Decarbonylation commenced and the evolved gases were collected in the inverted water-filled graduated cylinder or separatory funnel. Additional portions of peroxide were added intermittently whenever gas evolution subsided. The reaction was considered to be

complete when gas evolution had either stopped or had become interminably slow.

The volume of non-condensable gases was corrected to standard conditions taking into account the vapor pressure of water in the system. The yield of evolved gas was calculated on the basis of the volume of carbon monoxide expected on quantitative decarbonylation. For infrared spectroscopic analysis, the non-condensable gases were drawn off from the inverted separatory funnel through a calcium chloride drying tube into an evacuated 10-cm. gas cell, to which was attached a manometer to record the pressure of the gas in the cell. The gaseous products which had condensed in the Dry-Ice-cooled trap were analyzed directly by v-p-c, using either Column "A" (diisodecyl phthalate packing) or, in later experiments, Column "D" (tetraisobutylene packing - a special column for separation of low-molecular weight hydrocarbons). The analyses were performed at room temperature at operating pressures of 5-15 p. s. i. For infrared spectroscopic analysis samples of the condensed liquid were allowed to vaporize into a 10-cm. gas cell and the pressure of the gas in the cell was recorded on an attached manometer. Samples of the cooled liquid were transferred with cooled pipettes into n-m-r tubes for analysis by n-m-r and for storage. The residue in the reaction flask was usually distilled directly through a simple column and the fractions were analyzed by v-p-c, infrared spectroscopy and n-m-r.

In those experiments in which benzoyl peroxide was used as the initiator, the total amount of peroxide was placed in the reaction flask with the aldehyde and the solvent, before the flask was attached to the rest of the system. The mixture was then heated at the desired temperature and the rest of the procedure was as described above.

The only major changes in the procedure were made in the decarbonylation of 1-phenylcyclopropanecarboxaldehyde and dimethylcyclopropylacetaldehyde. In the former case, a tube was led directly from the reflux condenser to the inverted graduated cylinder without intermediate traps, since all products except carbon monoxide and methane, were expected to remain in the reaction flask. When the reaction was complete, the products were isolated by distillation of the material in the reaction flask. The procedure used for the decarbonylation of dimethylcyclopropylacetaldehyde will be described below.

Decarbonylation of Cyclopropanecarboxaldehyde. Three runs were made of the di-t-butyl peroxide-initiated decarbonylation of cyclopropanecarboxaldehyde, using aldehyde which had b.p. 95-98°, n_D^{25} 1.4264. In a typical run, 4.1 g. (0.059 mole) of cyclopropanecarboxaldehyde was dissolved in 37 ml. of redistilled diphenyl ether and the solution was treated with 4.3 g. (0.029 mole) of di-t-butyl peroxide as described above. The temperature of the mixture in the reaction flask was measured directly in this run. From an initial temperature of 138°, the temperature gradually dropped to 129° during the course of

the reaction. Gas evolution was sporadic, and only 190 ml. (14.4%) of gas was collected after 315 min. In another run, gas evolution amounted to 16.3% of theory after 1005 min. The infrared spectrum of the evolved gas showed it was mainly methane, by comparison with a spectrum of authentic material (152). There was only a small amount of carbon monoxide as shown by the pair of low-intensity peaks at 2110 cm^{-1} and 2170 cm^{-1} . No material condensed in the cold traps, indicating that little, if any, cyclopropane or other volatile hydrocarbon was formed. The material in the reaction flask on distillation gave a series of fractions which were analyzed by infrared spectroscopy and v-p-c. The low-boiling fractions contained acetone, t-butyl alcohol and recovered cyclopropanecarboxaldehyde and other unidentified components. Higher-boiling fractions consisted of cyclopropanecarboxaldehyde, cyclopropanecarboxylic acid and diphenyl ether, in addition to other minor unidentified components. The analyses indicate that the main product is cyclopropanecarboxylic acid in a yield of about 50%. In one run in which cyclopropanecarboxylic acid was isolated from the reaction products, it was ascertained with certainty that the acid was not initially present in the starting cyclopropanecarboxaldehyde.

In a run in which benzoyl peroxide was used as the initiator, at bath temperatures of 100-115°, gas evolution came to only 20% of theory. No material condensed in the cold traps and the residue was shown to consist mainly of benzene and recovered cyclopropanecarboxaldehyde.

Decarbonylation of 1-Methylcyclopropanecarboxaldehyde. Three

runs were made. In Runs I and II, the temperature in the reaction flask was measured directly and varied between 135-145° as the bath temperature was varied between 140-150° during the course of the reaction. In Run III, the bath temperature was maintained at 140±1° throughout. The aldehyde used had b.p. 104-105°, n_D^{25} 1.4261, and was indicated to be better than 99% pure according to v-p-c, which, however, as explained previously (see page 93) is not valid for testing the purity of this compound since the analytical data indicated that the aldehyde probably contained considerable amounts of peroxidized compounds. The experimental details were as follows:

	Run I	Run II	Run III
1-Methylcyclopropanecarboxaldehyde, g.	2.93	3.8	0.97
Di- <u>t</u> -butyl peroxide, g.	3.0	3.3	0.7
Diphenyl ether, ml.	30	40	10
Total reaction time, min.	520	675	1300
Gas evolution, %	58.7	58.9	60.0

No additional gas evolution occurred on addition of more peroxide or when the temperature was raised (Runs I and II). The infrared spectrum of the evolved gas showed that it was a mixture of methane and carbon monoxide, mostly the latter. An exact calibration of spectra of mixtures of these gases was not carried out. In all runs, liquid collected in the

cold trap; the exact amount could not be accurately measured because of the volatility of the product and amounted to about 0.5-1.0 ml. in Runs I and II, which corresponds to 30-40% of methylcyclopropane. Careful analysis of the liquid obtained in Run III by v-p-c on Column "D" showed only one peak (retention time 5.2 min. at 20°, 20 lbs. p.s.i., flow rate 180 cc/min.). The purity of the product is estimated to be at least 99.8%. The vapor infrared spectrum of condensed methylcyclopropane showed impurity bands due to carbon monoxide, carbon dioxide and methane, which were probably in the vapor phase in the cold trap above the condensed liquid. The rest of the spectrum was identical with that of methylcyclopropane as prepared by Mazur (109) by the reaction of 1,3-dibromobutane with zinc dust. The residue in the reaction flask was distilled in Runs I and II. The following fractions were obtained in Run I and were analyzed by v-p-c.

Fraction	Temp., °C	Wt., g.
I	70-90	2.3
II	90-92	0.30
III	100-105 (36 mm.)	0.35
IV	95-150 (40 mm.)	1.1

Fraction I consisted mainly of acetone and t-butyl alcohol containing a small amount of recovered 1-methylcyclopropanecarboxaldehyde.

Fraction II consisted of aldehyde and, t-butyl alcohol. Fraction III was

mainly 1-methylcyclopropanecarboxylic acid, identified by comparison of its infrared spectrum with that of authentic material as prepared by Cox (116). Fraction IV consisted of diphenyl ether containing a small amount of the above acid. The total yield of acid was 12-15%, based on the aldehyde taken in the decarbonylation reaction.

Decarbonylation of 1-Phenylcyclopropanecarboxaldehyde. The reaction was carried out with 2.47 g. (0.017 mole) of freshly distilled 1-phenylcyclopropanecarboxaldehyde, b.p. 92-94° (7.5 mm.), and 1.5 g. (0.010 mole) of di-t-butyl peroxide in the absence of solvent. The temperature in the reaction flask was maintained at 135-145°. Gas evolution was rapid and 420 ml. was collected after 1.5 hr., corresponding to 96.5% of theory. The residue was distilled in vacuo through a small distillation head to give the following fractions:

Fraction	Temp., °C	Wt., g.	\bar{n}_D^{25}
I	30-81 (35)	0.21	-
II	80-83 (35)	0.71	1.5292
III	80-67 (40-14)	0.51	-
IV	117-150 (0.5)	0.25	-

Fraction II consisted of 96% of one component, according to v-p-c. This component was also present in Fractions I (10%) and III (90%) and was identified as phenylcyclopropane on the basis of the following evidence. The physical properties of Fraction II agree best with those of phenylcyclopropane as compared with its open-chain isomers.

Compound	B.p., °C	$n_D(t)$	Ref.
Phenylcyclopropane	173-176	1.5285 (20°)	153
β -Methylstyrene	176-177	1.5903 (16°)	154
α -Methylstyrene	161-162	1.5384 (17.4°)	154
Allylbenzene	156-157	1.5110 (22°)	155

Direct comparison of v-p-c retention times of α - and β -methylstyrene with the components of Fractions II and III showed that the styrenes were entirely absent in these fractions; a mixture of all these substances was cleanly separated. The infrared spectrum of II showed no bands in the region $1600-1700\text{ cm}^{-1}$ but had a strong cyclopropyl band at 1020 cm^{-1} . It was later found that the infrared spectrum of the decarbonylation product was identical with that of phenylcyclopropane prepared by Caserio (54) by the Simmons-Smith reaction (72). Additional positive evidence for the structural assignment was obtained by the n-m-r spectrum of Fraction III which had a low-field resonance for the phenyl group and a series of resonances at high field characteristic of the ring protons of a mono-substituted cyclopropane. There were no resonances in the vinyl-proton region. There was an unidentified minor impurity with retention time 9.3 min. in the chromatogram of the phenylcyclopropane (retention time 5.8 min.) on analysis on Column "A" at 175° , flow rate 42 cc./min. The impurity amounted at most to 5% in Fraction III and only 1-2% in Fraction II, and may have been a contaminant in the original starting material. The total yield of phenylcyclopropane was about 55%.

Fraction IV solidified after distillation and the solid was recrystallized from hexane and had m.p. 83-85°. The infrared spectrum of the compound indicated it was a carboxylic acid and was later shown to be identical with the spectrum of authentic 1-phenylcyclopropanecarboxylic acid (lit. (113) m.p. 86-87°) prepared by hydrolysis of 1-phenylcyclopropanecarbonitrile (54). The yield of acid was 9.2%.

Decarbonylation of Cyclobutanecarboxaldehyde. Two runs were made using samples of cyclobutanecarboxaldehyde which were at least 98-99% pure by v-p-c, but which probably were contaminated with peroxidized compounds, according to analytical data (see page 136). One decarbonylation run will be described in detail, in which 0.86 g. (0.01 mole) of aldehyde (b.p. 106-110°, n_D^{25} 1.4311), 0.7 g. of redistilled di-t-butyl peroxide and 8 ml. of diphenyl ether were used. The bath temperature was maintained at 141±1° and 235 ml. of gas was collected over 1170 min., corresponding to 90.8% of theory. The infrared analysis of the non-condensable gas indicated it to be mainly carbon monoxide containing a small amount of methane. An estimated 300 mg. of liquid (55% of theory) was collected in the cold trap. Analysis of the liquid on Column "D" by v-p-c showed it was at least 98% of one component. Two minor peaks of low retention time corresponded to perhaps 0.01%. A peak of high retention time, corresponding to about 1-2% of the total, was shown to be due to acetone. 1-Butene was shown not to be present in the chromatogram. The main component was identified as cyclobutane by comparison of its infrared spectrum with that of an

authentic sample (156) while its n-m-r spectrum showed only a single unsplit resonance. A sharp singlet of low intensity appeared at slightly higher field with respect to the above resonance and is attributed to the acetone impurity. There were no other resonances in the spectrum.

Decarbonylation of Cyclopropylacetaldehyde. A number of runs were made under various conditions. In most of the runs, the aldehyde used appeared to be at least 99% pure, according to y-p-c, but must have been contaminated with peroxy compounds, according to the analytical data (see page 129). In a typical experiment, 1.74 g. (0.020 mole) of cyclopropylacetaldehyde, n_D^{25} 1.4207, was dissolved in 20.4 g. of redistilled diphenyl ether, to which was added 3.0 g. (0.0205 mole) of di-t-butyl peroxide. The temperature of the liquid in the flask was maintained at 133-136° during the reaction. Gas evolution was as follows:

Elapsed time, min.	Vol. of gas collected, ml., at 26.0°, 741.0 mm.
20	141
45	244
60	338
90	446
120	508

The volume of gas amounted to 94.2% of theory and consisted of carbon monoxide containing a small amount of methane. Approximately 0.8-1.0 g. of liquid collected in the cold trap. This liquid had only one peak in

its vapor-phase chromatogram of retention time 4.1 min. on Column "A" at room temperature, 5.5 p.s.i., flow rate 10 cc./min. The material is estimated to be at least 99.9% pure, and was identified by comparison of its infrared and n-m-r spectra and y-p-c retention time with those of an authentic sample of 1-butene obtained commercially.

Two runs were made of the decarbonylation of cyclopropylacetaldehyde, n_D^{25} 1.4167, without solvent, initiated by di-t-butyl peroxide. In both runs, gas evolution was slow and sporadic, as compared with the runs above. In one run, about 50% of the theoretical amount of carbon monoxide was collected over 9.5 hr. before gas evolution stopped completely as the aldehyde and di-t-butyl peroxide were heated at 130-140°. Only a very small amount of liquid collected in the cold trap, the y-p-c retention time of which was identical to that of authentic 1-butene. There was again only one peak in the chromatogram.

One run was made of the decarbonylation of cyclopropylacetaldehyde (0.69 g., 0.0082 mole) with benzoyl peroxide (1.00 g., 0.0041 mole) at 81±1° without solvent. Gas evolution was quite vigorous and after 12 min. the condenser was suddenly blown off the flask and simultaneously the residue turned very dark. By this time 130 ml. of gas (31% of theory) had collected. There was a small amount of liquid in the cold trap which had one peak in its vapor-phase chromatogram, with a retention time identical to that of pure 1-butene. In another run in which benzoyl peroxide initiated decarbonylation of a solution of

0.57 g. (0.0068 mole) of the aldehyde in diphenyl ether, about 60% of the theoretical amount of carbon monoxide collected over a period of 68 hr. This gas was shown to be a mixture of carbon monoxide and carbon dioxide by infrared analysis. However, no liquid collected in the cold trap. The residue was distilled in vacuo and only 80 mg. of liquid was collected, the infrared spectrum of which was similar to that of cyclopropylacetaldehyde. A few extra bands indicated the presence of minor impurities.

One run was made of the decarbonylation of an analytically pure sample of cyclopropylacetaldehyde (0.47 g., 0.0056 mole) which had n_D^{25} 1.4182 after redistillation in a nitrogen atmosphere and which, therefore, presumably contained no peroxidic impurities. The reaction, initiated by 0.3 g. of di-t-butyl peroxide, was carried out in 5 ml. of diphenyl ether at $141 \pm 1^\circ$. Over a period of 345 min., 110 ml. of gas (76.5%) was collected and was shown to consist of carbon monoxide and carbon dioxide containing only a very small amount of methane. The condensate in the cold trap amounted to approximately 50 mg., and showed a single peak in its vapor-phase chromatogram, with a retention time identical to that of pure 1-butene.

Decarbonylation of Isovaleraldehyde. To 8.4 g. of redistilled isovaleraldehyde (b.p. 88° , n_D^{25} 1.3880) in 25 ml. of redistilled diphenyl ether, heated in an oil bath at 140° , was added 7.3 g. (0.1 mole) of di-t-butyl peroxide. Over a period of 310 min., 2250 ml. of gas (91% of theory) was collected. The liquid isolated in the cold trap

amounted to 3.6 g. (62% of theory). There were two peaks in the vapor-phase chromatogram of this material, and their areas were in the ratio 10:1. The larger peak is undoubtedly due to isobutane since the infrared spectrum of the mixture is almost identical with that of pure isobutane. There is a band at $950-970\text{ cm}^{-1}$ which suggests an olefinic impurity. However, v-p-c analysis of this mixture with added isobutylene on Column "D", in which the three components were separated, indicated that the unknown impurity in the isobutane is not isobutylene.

Several experiments were run in which decarbonylation was initiated by benzoyl peroxide at 80° . When the liquid aldehyde was used, the gas evolution came to 16.5% and 17.4% of theory in two runs, and it consisted of a mixture of carbon monoxide and carbon dioxide. The small amount of material collected in the cold trap was shown to consist of isobutane and the unknown component, as described above. Similar results were obtained when the decarbonylation was carried out in chlorobenzene and in diphenyl ether.

Decarbonylation of a Mixture of Cyclopropylacetaldehyde and Isovaleraldehyde. This experiment utilized 0.43 g. (0.005 mole) of cyclopropylacetaldehyde (n_D^{25} 1.4180), 0.43 g. (0.005 mole) of redistilled isovaleraldehyde (b.p. 90° , n_D^{25} 1.3879) and 8 ml. of diphenyl ether, to which was added 0.5 g. of di-t-butyl peroxide. The reaction flask was heated in a bath at $141\pm 1^\circ$. After 120 min., 125 ml. of gas (44% of theory) was collected. The reaction was stopped by quickly

removing the reaction flask from the oil bath. There was about 200 mg. of liquid in the cold trap. Analysis by v-p-c (Column "D", 25°, 6 p.s.i., flow rate 20 cc./min.) showed the presence of three components: 1-butene, isobutane and the unknown product derived from isovaleraldehyde (see above) in ratios of 36:51:13, respectively. The chromatogram was previously calibrated with 1-butene and the isobutane mixture.

In a second experiment, 4.0 ml. of cumene was added to a mixture of 0.60 g. each of isovaleraldehyde and cyclopropylacetaldehyde in 10 ml. of diphenyl ether, to which was then added 1.5 g. of di-t-butyl peroxide. The reaction was again carried out in a bath at 141±1° and was stopped after 50 min. when 150 ml. of gas (40.4% of theory) had been collected. The material in the cold trap (200 mg.) was analyzed as above and consisted of the same three components in a ratio of 46:42:12, respectively.

Decarbonylation of Dimethylcyclopropylacetaldehyde. Two runs were made of this reaction using aldehyde which had been freshly distilled under nitrogen. The experimental set-up was similar to that described previously, page 144, except that the condenser attached to the reaction flask was not water-cooled and was fitted with a glass take-off tube leading to a Dry Ice-cooled receiver. Rubber tubing led from the receiver through a trap to the gas-measuring apparatus. The details of the two runs are tabulated below.

	Run I	Run II
Dimethylcyclopropylacetaldehyde, g.	1.20	0.50
Dimethylcyclopropylacetaldehyde, moles	0.0112	0.00445
Di- <u>t</u> -butyl peroxide, g.	1.0	0.3
Bath temperature, °C	144+1	135+1
Total reaction time, min.	360	85
Volume of gas evolved, ml.	158	55
% of theoretical amount of carbon monoxide	53.8	47.2
Amount of material collected in cold trap, mg.	440	100-200

At the end of the time indicated above, gas evolution had stopped completely and did not recommence on addition of more peroxide. During the course of the reaction, some low-boiling material distilled up through the condenser and was collected in the cold trap. When the reaction was finished, nitrogen was passed through the system to carry any additional quantities of products into the cold trap. Analysis of the condensate by v-p-c (Column "A", 40°) indicated the presence of several components. Recovered di-t-butyl peroxide and t-butyl alcohol were indicated to be present and apparently there was little or no acetone in the mixture. The main component had a retention time identical to that of 2-methyl-2-pentene (obtained from Phillips Petroleum Co.) while there was no peak with a retention time corresponding to that of the unresolved mixture of isopropylcyclopropane and 2-methylpentane (see page 142).

In Run I, the mixture was distilled to separate the hydrocarbon product from the other components. However, the distillate still contained some t-butyl alcohol as determined by v-p-c and also by the presence of a broad band at 3400 cm^{-1} in the infrared spectrum of the mixture. Except for bands at 1200 cm^{-1} and 915 cm^{-1} , also due to t-butyl alcohol, the infrared spectrum of the distilled decarbonylation product is identical to that of 2-methyl-2-pentene obtained commercially. The n-m-r spectrum of the distillate is identical in all details with that of authentic 2-methyl-2-pentene except for a low-field intensity singlet and a high-intensity singlet in the region characteristic of methyl protons; the resonances are the expected ones for the hydroxylic and methyl protons of t-butyl alcohol. Some of the residue from the decarbonylation reaction was distilled in Run I. According to v-p-c, the distillate (0.82 g.) consisted mainly of recovered di-t-butyl peroxide and a small amount of dimethylcyclopropylacetaldehyde, in addition to numerous trace components which were not identified. The tarry residue from the distillation was discarded.

The decarbonylation of dimethylcyclopropylacetaldehyde was also carried out in diphenyl ether. The bath temperature was maintained at $140\pm 1^\circ$ as 141% of the theoretical amount of gas was collected. The gas consisted of carbon monoxide and carbon dioxide and contained no methane, according to infrared analysis. No explanation can be given for the large amount of evolved gas. The decarbonylation products were separated from diphenyl ether by heating the mixture in a

bath at 190°. The distillate was analyzed by v-p-c and n-m-r and was indicated to be a mixture of the same components as reported in the runs above.

In a final run, the decarbonylation of 0.89 g. (0.0079 mole) of freshly distilled dimethylcyclopropylacetaldehyde, n_D^{25} 1.4242, was run in 1.5 ml. of benzyl mercaptan, at a bath temperature of 135±1°. Gas evolution amounted to 55.4% of theory over 120 min. No further gas was evolved thereafter. The infrared spectrum of the gas indicated it was carbon monoxide containing only traces of carbon dioxide and methane. The liquid in the cold trap amounted to 0.46 g. Analysis of this liquid by v-p-c indicated that it contained, in addition to 2-methyl-2-pentene, t-butyl alcohol and a small amount of di-t-butyl peroxide, as obtained previously, a component having the same retention time as that of an unresolved mixture of isopropylcyclopropane and 2-methylpentane. Additional evidence for the composition of the decarbonylation product was obtained from its n-m-r spectrum. The spectrum was basically that as described on page 159 with some differences which are ascribable to the presence of isopropylcyclopropane in the mixture. In particular, the two high-field resonances found in the spectrum of isopropylcyclopropane and previously assigned to the ring-proton resonances (see page 143) were also found in the spectrum of the present decarbonylation product. From the vapor-phase chromatogram, the hydrocarbon portion of the mixture consisted of 82% 2-methyl-2-pentene and 18% isopropylcyclopropane.

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V. PROPOSITIONS

1. It has been observed that the hydrocarbon product of decarbonylation of cyclopropylacetaldehyde at 130-140° is exclusively 1-butene, while mixtures of cyclic and open-chain products are produced on photochlorination of methylcyclopropane (1). The results of the photochlorination experiments are complicated by numerous side reactions; the temperature during the reaction is also not known with certainty. It would be desirable to study the variation in product composition, as a function of temperature, in the free radical reaction of a suitable cyclopropylcarbinyl derivative, preferably over a wide range of temperature. The reaction of mercaptans with trialkyl phosphites, induced either by ultraviolet irradiation or by the decomposition of a radical chain initiator, produces hydrocarbons by a process for which a radical chain mechanism seems well-substantiated (2). By this reaction, alkyl radicals of known structure can be generated from the corresponding mercaptans over a fairly large range of temperatures. It is therefore proposed that the nature of the product(s) from the reaction of cyclopropylcarbinyl mercaptan and triethyl phosphite be determined as a function of temperature.

2. It has been proposed (2) that the mechanism of production of hydrocarbons from the reaction of mercaptans and dialkyl peroxides with trialkyl phosphites involves attacks of alkoxy and thiyl radicals on the phosphite molecule to give a transient phosphoranyl radical; decomposition

of the phosphoranyl radical then gives alkyl radicals and trialkyl phosphorothionate and phosphite, respectively. The driving force for the latter reaction is said to be the formation of very strong semi-covalent P-S and P-O bonds. Whereas the radical decomposition of diacyl peroxides usually affords carbon dioxide and alkyl radicals, it is suggested that alkyl radicals and carbon monoxide might be produced if the decomposition were carried out in the presence of trialkyl phosphite. Such a reaction might be useful for the generation of alkyl radicals which are not particularly stabilized from diacyl peroxides at lower temperatures than are customary in the usual thermal decomposition reactions.

3. Richards and Hill (3) have reported data demonstrating great solvolytic reactivity of α -metallocenyl acetates. The solvolysis rates are of the same order of magnitude as for trityl acetate. Included in this study were non-constrained α -ferrocenylcarbinyl acetates as well as a system in which the site of reaction was in a three-membered heteroannular bridge. Trifan and Bacskai (4) have reported solvolysis rates of exo- and endo- α -acetoxy-1,2-tetramethylene ferrocene. The exo isomer solvolyzed 2240 times as fast as the endo isomer. Similar results have been obtained independently by Richards and Hill (5) and are explained by backside participation of the iron orbitals, thus aiding solvolysis of the exo, but not the endo, isomer. The enhanced solvolysis rates in general reflect the great ability of a ferrocene nucleus to stabilize an α -cationic center. The rates of solvolysis of ferrocenylcarbinyl acetates studied thus far must reflect, to some extent, a combination of both these effects. It is therefore proposed that a study be made of the rates of

solvolysis of α -ferrocenylcarbinyl derivatives in which the site of reaction is located in a homoannular bridge between C_1 and C_3 on the cyclopentadiene ring. The site of reaction in such a compound should be too far removed from the iron atom for direct participation by the iron orbitals to be at all important. Although coplanarity of the cationic center with the ferrocene ring, as required for maximum resonance stabilization, should be impossible if the bridge is short enough, some stabilization by the ring should still be important and measurable.

Although the synthesis of the desired compounds is not anticipated to be easy, two routes seem possible. Pyrolysis of metal salts of ferrocene-1,3-bis-carboxylic acids (6) may afford cyclic ketones. Alternatively acyloins could be formed from ferrocene-1,3-bis-carboxylic esters. Appropriate manipulation of the functional groups would give alcohols from which the desired acetates could be prepared. Since it has been determined that at least nine carbon atoms are needed to form a bridge between the para positions of benzene (7), it would be interesting to determine the number of carbons necessary to form a bridge between C_1 and C_3 of ferrocene.

4. In order to determine the applicability of the method of competitive decarbonylation of aldehydes (8) to the determination of the relative stability of intermediate radicals, the following experiments are proposed.

(a) Calibration of the procedure by generation of a known resonance-stabilized radical in competition with a non-delocalized radical

would be desirable. Thus, competitive decarbonylation of a 1:1 mixture of phenylacetaldehyde and a typical aliphatic aldehyde, such as n-decanal, carried to about 50% completion, and determination of the ratio of the products derived from each aldehyde, should provide information as to the relative rates of chain-propagation steps in these two cases.

(b) It is assumed implicitly above that rates of chain initiation are approximately the same for phenylacetaldehyde and for typical aliphatic aldehydes and, by extension, for all aldehydes. While this is reasonable, it can be checked experimentally. Treatment of mixtures of aldehydes with radical chain initiators in carbon tetrachloride, which effectively traps the initially formed acyl radicals (9), and determination of the extent of formation of the corresponding acyl chlorides, would measure the relative rates of hydrogen abstraction from the respective aldehydes. This might provide information as to relative aldehyde C-H bond dissociation energies as a function of the structure of the aldehyde.

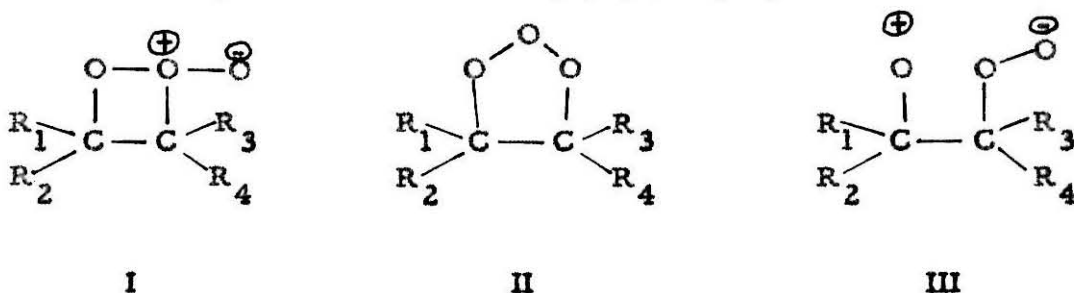
5. The solvolysis of 1,4-dihydrobenzyl *p*-toluenesulfonates in acetic acid at 90° in the presence of sodium dihydrogen phosphate monohydrate has been reported (10) to give small amounts of alkylbenzenes and mainly alkylcycloheptatrienes. Since there is some doubt as to the distribution of the various alkylcycloheptatrienes in the product, because of subsequent isomerization, determination of the equilibrium proportions of the various cycloheptatrienes would be desirable. In addition, it would be interesting to determine the nature of the products of solvolysis under less acidic conditions. As homoallylic participation seems highly likely

in the 1,4-dihydrobenzyl system, it would be valuable to obtain accurate kinetic data to compare with similar data in other systems which are known to solvolyze with homoallylic participation.

6. Solvolysis reactions which proceed formally through 1,4-dihydrobenzyl cations are known to give rise to mixtures of six-membered and seven-membered ring products (10). Since homoallylic participation in this system seems quite likely, and since it is known that homoallylic radical intermediates are predicted by simple molecular orbital theory to be stable (11), it would be interesting to determine the products of a free radical reaction of a 1,4-dihydrobenzyl derivative. The intermediate radicals might react without rearrangement or might react with rearrangement to give cycloheptadienyl or bicyclo[4.1.0]heptyl derivatives or mixtures of these products. Initially, the radicals could be generated from 1,4-dihydrobenzyl mercaptan (2) or by decarbonylation of 1,4-dihydrophenylacetaldehyde.

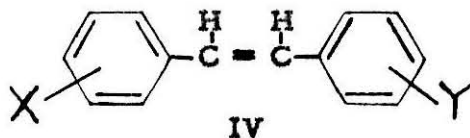
7. While many of the mechanistic details of the ozonization of unsaturated compounds have been elucidated, principally through the elegant researches of Criegee and co-workers, several problems still remain unsolved (12). It appears well-established that a "primary" ozonide is formed and that this fragments into a carbonyl compound and a zwitterion, which then recombine to give the isolable ozonide in the usual reaction. However, there is considerable dispute as to the mechanism of formation of the "primary" ozonide, the structure of this intermediate and the factors which

determine the direction of cleavage of the "primary" ozonide, that is, which moiety becomes the carbonyl fragment and which becomes the zwitterion (12,13). If the structure of the "primary" ozonide is I, the latter question is decided in the formation of I, while if it is II, the question is decided in the decomposition of II. Bailey (12) has proposed a mechanism involving



initial formation of a π -complex between ozone and the olefin, the mode of collapse of which to give III is determined primarily by the inductive effects of R_1 , R_2 , R_3 and R_4 . While this theory is supported by most of the available (but scanty) data, there are exceptions to this generalized mechanism. In particular, the importance of resonance effects in the Bailey mechanism seems to be underestimated. The following experiments are proposed to shed more light on these problems.

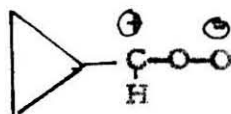
(a) Ozonization of a series of substituted stilbenes IV in methanol



should give two products: a substituted benzaldehyde and a substituted α -methoxyhydroperoxide (derived from attack of methanol on the zwitterion intermediate). Determination of the extent to which each of the substituted phenyl groups ends up in each of the two possible products as X and Y are

varied widely, so as to include a variety of electron-withdrawing and electron-supplying groups, should give information as to the relative importance of inductive and resonance effects in determining the mode of formation of the fragments derived from the "primary" ozonide.

(b) If the Bailey mechanism of ozonolysis is correct, ozonolysis of 1-cyclopropylpropene in methanol should give cyclopropanecarboxaldehyde and 1-methoxyethyl hydroperoxide. However, if resonance effects are important, the products should be acetaldehyde and the hydroperoxide derived from zwitterion V.



V

Since rearrangements are known to occur in carbonium ion reactions of cyclopropylcarbinyl derivatives (14), rearrangements might occur on ozonolysis of vinylcyclopropanes if structure V or a similar ion is an intermediate. Cyclopropanecarboxaldehyde was a product of ozonolysis of vinylcyclopropane, although it was isolated in only 8% yield (15); no mention was made of any rearranged products.

8. Free radical decarbonylation of cyclopropylacetaldehyde and cyclopentylacetaldehyde yields exclusively ring-opened and cyclic hydrocarbon products, respectively (16,17). The addition of carbon tetrachloride to β -pinene in the presence of benzoyl peroxide resulted in a rearranged product (18) which is derived formally from ring opening of a substituted cyclobutylcarbinyl radical. It would therefore be of interest

to determine the fate of unsubstituted cyclobutylcarbinyl radicals as generated by decarbonylation of cyclobutylacetaldehyde. If ring opening is observed, the reaction should also be carried out in the presence of benzyl mercaptan.

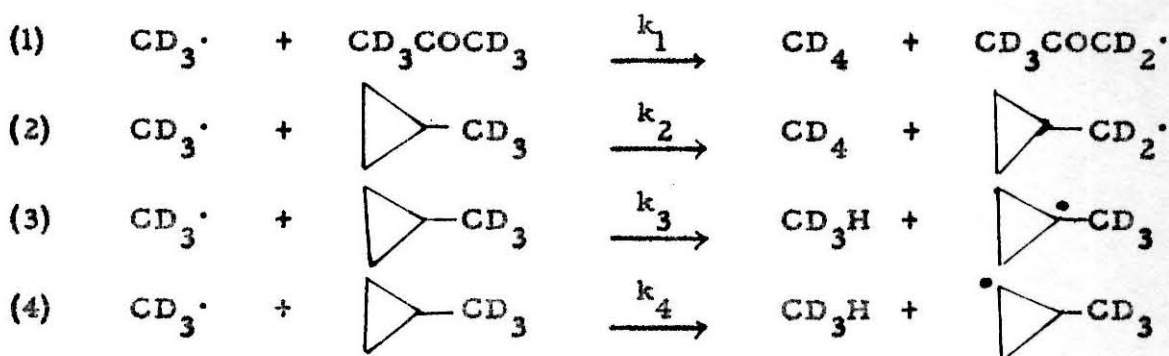
9. There is only one report in the literature of the preparation of a quaternary ammonium cyanide (19) and no analytical data are reported for this compound. Attempts to prepare such salts by standard procedures were not successful (20). Such salts may be preparable through the use of anion exchange columns. Columns which serve as sources of cyanide ion have not been studied extensively, but it should be possible to prepare such columns by standard procedures. Passage of a solution of a quaternary ammonium iodide or a quaternary base through such a column might result in anion exchange. The salt could then be isolated from the solution by usual methods.

Quaternary ammonium cyanides might prove to be useful in the preparation of nitriles in non-aqueous media. In addition, such salts might be useful in studies of the nucleophilic reactivity of cyanide ion in comparison with halide ions and other nucleophiles. The relative reactivity of alkali halide salts has recently been found to be misleading in this respect (21).

10. It has been suggested (22) that the radicals derived from cyclopropylcarbinyl derivatives may have enhanced stability due to the formation of "non-classical" homoallylic structures. If this is true, the activation energy for hydrogen abstraction from the methyl group of

methylcyclopropane should be less than for abstraction from other hydrocarbons to give non-delocalized primary radicals. The activation energy for abstraction of a primary hydrogen from *n*-butane by CD_3 radicals has been determined to be 11.4 kcal./mole (23). It is proposed that a similar procedure be employed to determine the activation energy for primary hydrogen abstraction from methylcyclopropane.

Because of the general lack of selectivity of methyl radicals, the following scheme is suggested, based on the earlier procedures (23). In the photolysis of mixtures of acetone- d_6 and trideuteromethylcyclopropane, the following reactions would be expected to be most important:



Experimentally, the ratio of $\text{CD}_4/\text{CD}_3\text{H}$ would be measured mass spectrophotometrically at very low reaction conversions (1 or 2%). At this stage of the reaction, the ratio of the rates of production of CD_4 and CD_3H would be given by

$$(5) \quad \frac{R_{\text{CD}_4}}{R_{\text{CD}_3\text{H}}} = \frac{\text{CD}_4}{\text{CD}_3\text{H}} = \frac{k_1 A + k_2 B}{k_3 B + k_4 B} = \frac{k_1}{k_3 + k_4} \frac{A}{B} + \frac{k_2}{k_3 + k_4}$$

where $A = \text{CD}_3\text{COCD}_3$ and $B = \triangle - \text{CD}_3$. At a given temperature, determination of $\text{CD}_4/\text{CD}_3\text{H}$ at various initial ratios of A/B would permit determination of the ratios $\frac{k_1}{k_3 + k_4}$ and $\frac{k_2}{k_3 + k_4}$. If we set $k_3 + k_4 = k_x$,

it is clear that determination of these ratios at at least three temperatures permits calculation of the differences in activation energy $E_1 - E_x$ and $E_2 - E_x$. Since E_1 is known to be 11.3 kcal./mole (23), E_2 can then be calculated.

Determination of the ratio of CD_4/CD_3H on photolysis of acetone- d_6 and undeuterated methylcyclopropane, in combination with information obtained above with the deuterated hydrocarbon, would then permit calculation of the energy of abstraction of primary hydrogen from methylcyclopropane.

11. For the last two years, a number of graduate students and post-doctoral fellows in the Chemistry Department have created and appeared in a musical play, presented at the annual Chemistry Department Christmas party. Both these presentations, in which the idiosyncrasies of the faculty, students and shop workers were gently and affectionately spoofed, met with enthusiastic acclaim from the faculty, students and more objective observers. It is proposed that a serious attempt be made on the part of the faculty and students to keep this tradition alive. It is important that the people in the Chemistry Department be occasionally reminded of how they appear to others lest they succumb to the great danger of taking themselves too seriously.

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